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AMERICAN LEATHER CHEMISTS ASSOCIATION

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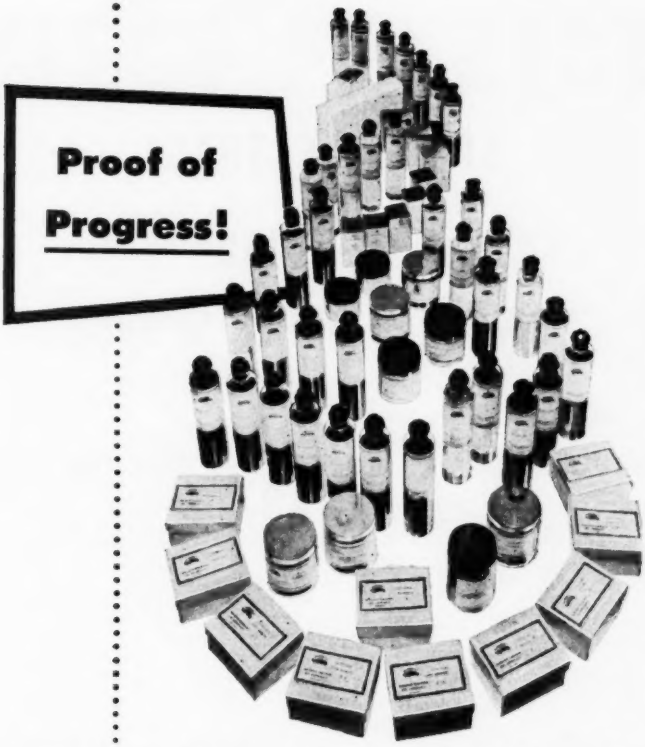

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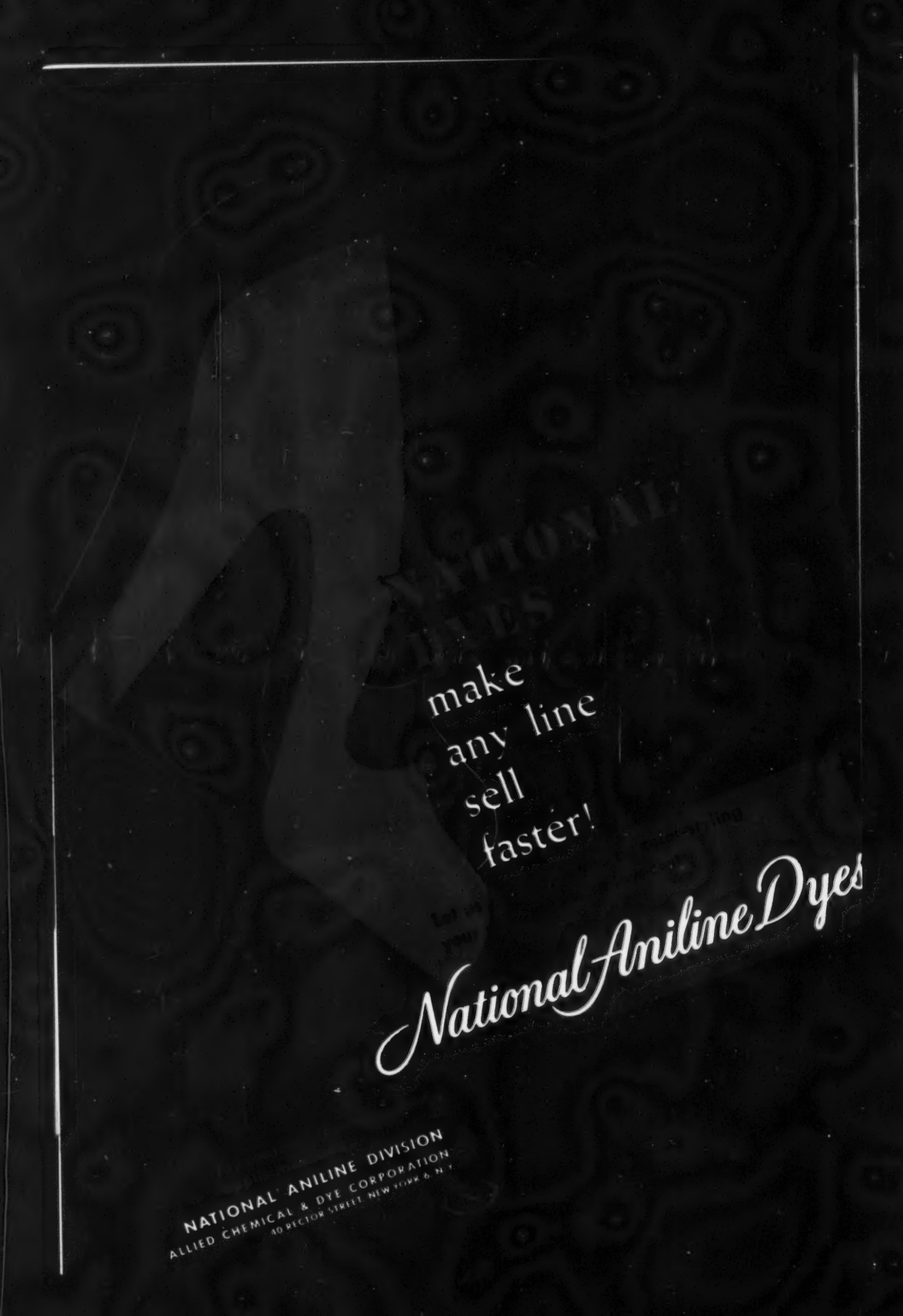
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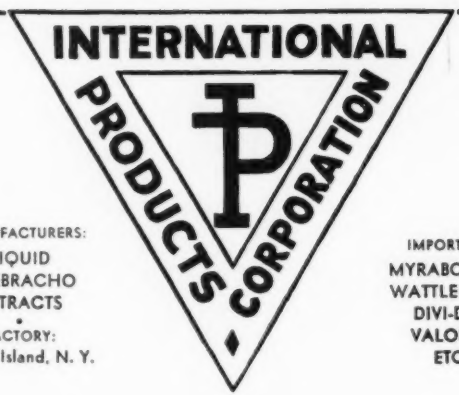

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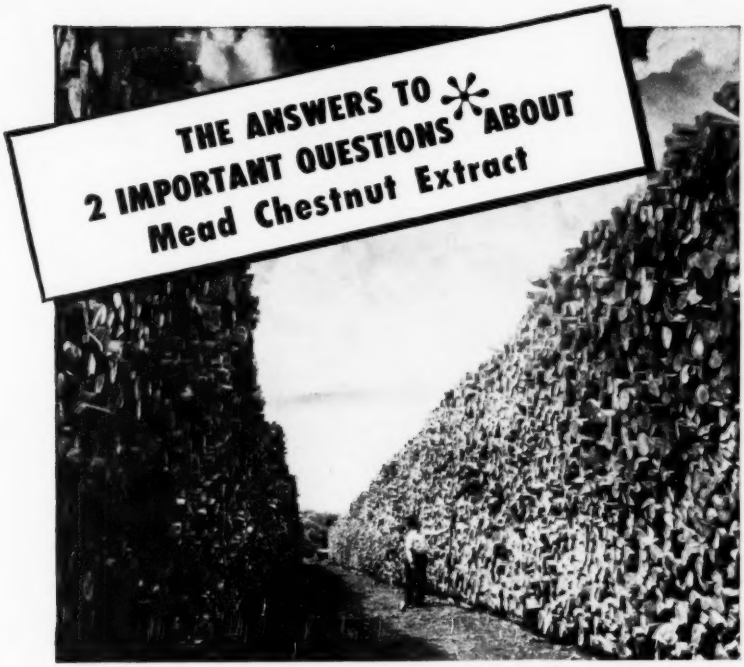

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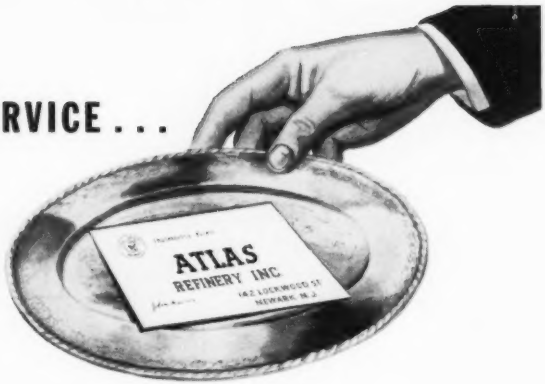

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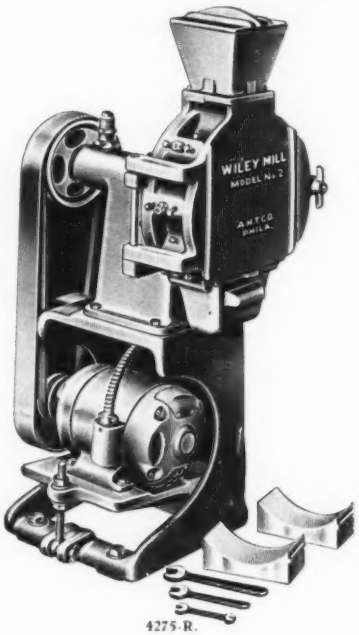

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JOHN EDWIN VAREY

John E. Varey, a member of our Association since 1947, died suddenly on January 1st, 1951. Mr. Varey was formerly assistant superintendent of the C. F. Hyman Company of London, Ontario. He later joined the B. D. Eisendrath Tanning Company of Racine, Wisconsin, as assistant superintendent, becoming superintendent in 1947. Mr. Varey was recognized for his leadership and his knowledge of leather and tanning.

Determination of Grease in Leather

By E. W. Zimmerman and E. F. Pangborn

National Bureau of Standards
Washington, D. C.

I. Introduction

In the analysis of leather, those constituents commonly referred to as "grease" are determined by extracting 10 grams of ground leather with a solvent. According to Federal Specification KK-L-311, petroleum ether boiling below 80°C shall be used unless otherwise specified. According to MIL-L-3122, Leather Upper Chrome Retan (grain out) (chrome-vegetable retan), chloroform is specified as the solvent for the removal of grease. The work described here is confined to the use of petroleum ether and chloroform because these are the only solvents used in this laboratory for the determination of grease in leather. The extraction is conducted in a soxhlet extractor at such a rate that the time required to complete one cycle shall be 15 ± 3 minutes. Twenty cycles, which requires 5 hours, are considered sufficient to remove all of the extractable material.

In a recent study on the sampling of sides for upper leather, it was necessary to make chemical analyses on about 300 samples of leather. Chloroform was specified to determine the grease, which varied from 25 per cent to 50 per cent depending upon the locations from which the sample was taken. It was found that the usual extraction time of five hours had to be increased to eight hours in order to remove all of the extractable material, and that the large quantities of grease obtained required drying for approximately three hours at 100°C in order to obtain constant weights ($\pm .002$g). Consequently, an investigation was made to develop a shorter and simpler procedure. The method described herein is the result of this study. Relatively small specimens are extracted in metal thimbles for a shorter period of time without sacrificing the accuracy obtained by the use of larger specimens.

II. Extraction Equipment

The equipment used is the same as that employed for the extraction of rubber samples*, and can be obtained from the suppliers of scientific equip-

*ASTM Standard D-297, 43T Chemical Analysis of Rubber Products.

ment. The apparatus consists of a block tin condenser, a 400 ml wide mouth erlenmeyer flask, and a pyrex siphon cup which are assembled as shown in Figure 1. A metal thimble, shown in Figure 2, is used to hold the specimen.

The metal thimble consists of a brass tube about 62 mm long, having an outside diameter about 1 mm less than the inside diameter of the siphon cup.

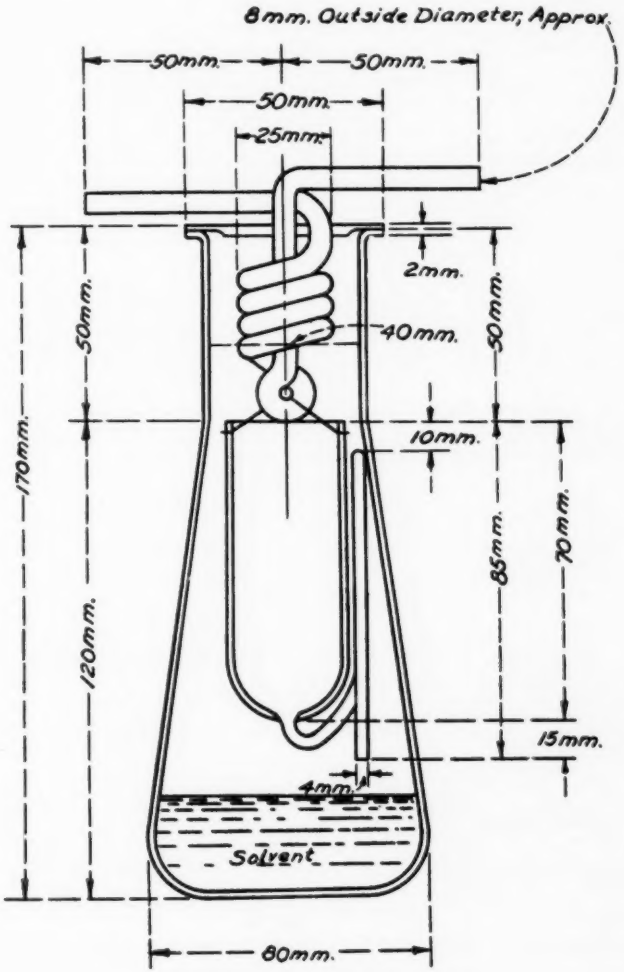

FIGURE 1.—Extraction Equipment.

The bottom edge of the tube is pressed in at one place in order to avoid having a liquid seal when the thimble is assembled in the siphon cup. A depression approximately 4 mm deep, extending up the side of the tube for approximately 10 mm is satisfactory. A piece of 100 mesh screen is soldered to the bottom of the tube. The entire thimble can be nickel-plated if desired, by using the electroless process*.

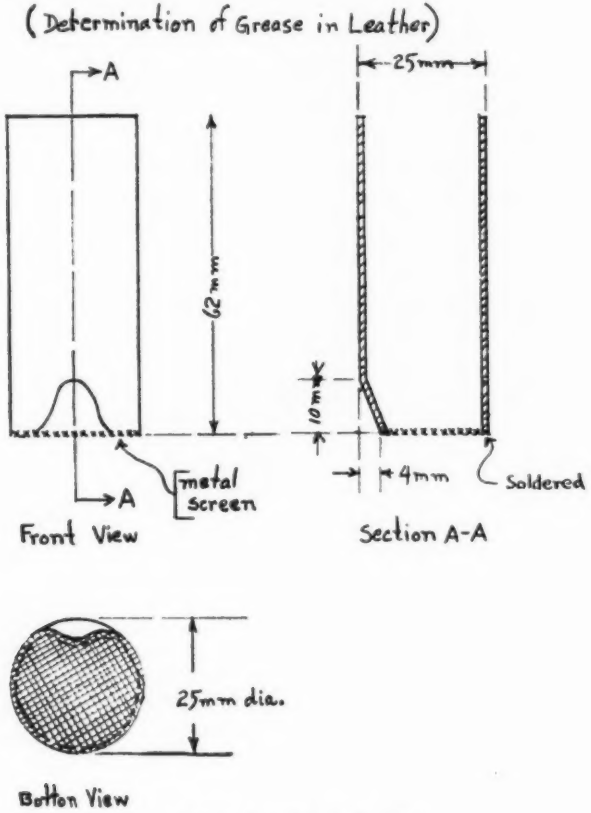

FIGURE 2.—Metal Thimble.

III. Procedure

A specimen of approximately 3 grams, previously ground in a Wiley mill to pass through a 4 mm screen, is weighed to the nearest 10 mg. A thin layer

*NBS Journal Research 39, 1947, Research Paper RP1835.

of fat free absorbent cotton is placed in the bottom of the metal thimble to keep the ground leather from plugging the screen. The weighed specimen is then transferred to the thimble and another plug of cotton placed on top. The metal thimble is then placed in the siphon cup and the cup suspended under the condenser.

An extraction flask, previously dried for an hour at 100°C and cooled, is weighed, sixty ml of chloroform transferred to it, and the flask is then assembled with the condenser as shown in Figure 1. Sufficient heat is applied to the flask so that the siphon cup is filled and emptied once every two to three minutes. After extracting for two hours, the flask is removed, and the solvent evaporated on a steam bath, using a current of air to prevent boiling. When the solvent has been removed, as indicated by the absence of the odor of chloroform, the flask is removed from the steam bath, dried to constant weight (0.002 g) in an oven at 100°C, cooled and weighed.

IV. Development of Method

Preliminary experiments were made using chloroform to extract grease from chrome-tanned stuffed leather containing about 37 per cent grease. Five-gram specimens were used for this work, using the ASTM rubber extraction equipment.

Several methods of confining the leather specimen in the siphon cup were tried. When the leather was put directly into the cup on top of a cotton plug, the vaporization of the solvent in the lower portion of the cup caused the leather to rise until it protruded above the top of the siphon cup. Inserting a circular piece of wire gauze beneath the cotton plug did not prevent this from occurring. Apparently it is necessary to provide a channel to permit the vapor formed at the bottom of the siphon cup to escape. A loosely fitting thimble will provide this channel, and prevent the specimen from being pushed up.

Commercially available cellulose thimbles to hold the specimen were not considered satisfactory from the standpoint of speed of extraction because of the possibility of the solvent passing out through the side of the thimble when the siphon cup was either being filled or discharged. If, however, a metal thimble is used, all the solvent that drips from the condenser must pass through the leather specimen before it can be discharged by the siphon cup. The siphon cup with the metal thimble containing 5 grams of dry leather requires approximately 27 ml of solvent to fill it to the point where it will siphon, and then only 7 ml are discharged, the remaining 20 ml being retained by the leather. Thus for efficient extraction it is essential that the subsequent distillate be prevented from by-passing the leather in the bottom of the thimble by passing out through the sides of the thimble, as would be the case if paper thimbles were used. Metal thimbles dented at the bottom edge proved to be more efficient than cellulose thimbles.

Four samples of leather were selected to carry out the experimental work to determine the time necessary for complete extraction and the effect of specimen size. These samples and the amount of chloroform extractable material they contain, as determined by the method described in Federal Specification KK-L-311, are described as follows:

Sample No.	Description	Chloroform Extract
1	chrome tan, stuffed	41.52
2	chrome retan, stuffed	29.50
3	vegetable-tanned sole	4.66
4	fat liquored chrome retan	14.13

The samples were ground in a Wiley mill to pass through a 4 mm screen, then spread out in a thin layer in a tray and kept in an atmosphere of 65 per cent relative humidity at 70°F for several days, after which each was thoroughly mixed, bottled, and stored at these same conditions.

In order to determine the time required for complete removal of the grease with rubber extraction equipment, five-gram specimens of each of the four leather samples were extracted with chloroform for two hours, followed by two more extractions of one hour each, using fresh solvent in a clean flask for each extraction. The amounts of grease removed during the various intervals are as follows:

	Sample			
Extraction time, hr.	1	2	3	4
2	41.40	29.61	4.82	14.16
3	0.06	0.06	0.02	0.12
4	0.04	0.04	0.02	0.14

These results show that an extraction for two hours with chloroform removes over 99 per cent of the extractable material from samples 1, 2, and 3, and 98 per cent from sample 4. A comparison of these results with those obtained by the procedure described in Federal Specification KK-L-311 shows that a two-hour extraction period is sufficient when chloroform is used as the solvent.

In order to determine the rate of extraction with petroleum ether, samples Nos. 1 and 3 were extracted in a similar manner with three portions of petroleum ether. An additional extraction for one hour, using chloroform, was made in order to determine the amount of material that was not removed by the petroleum ether. In this experiment, one and five gram specimens of each sample were used, and the results are as follows:

		Sample 1		Sample 3	
		1 g	5 g	1 g	5 g
Petroleum ether,	2 hr	38.85	39.62	3.96	4.12
do.	3rd hr	0.18	0.06	0	0.02
do.	4th hr	0.01	0.03	0	0.01
Chloroform,	5th hr	0.95	0.78	0	0.16
Total		39.99	40.49	3.96	4.31

These results indicate that a period of two hours was sufficient to remove 99 per cent of the material extractable with petroleum ether. However, this solvent did not remove all of the extractable material as shown by a subsequent extraction of the same specimen with chloroform.

The additional material removed by chloroform had the appearance of grease, and it was insoluble in water. In acetone the residue was strongly fluorescent. The difference in the behavior of chloroform and petroleum ether has been adequately treated by previous authors (*) (†), and it is not the intent of the present study to enlarge upon their findings.

In order to determine for each of the four samples of leather and for each of the two solvents, the effect of sample size on the observed grease content as well as the reproducibility of the results, an experiment was performed on the basis of a statistical design.

Specimens weighing 1, 2, 5, and 10 grams were used in the tests. The 1, 2, and 5-gram specimens were extracted by using the rubber extraction equipment with the metal thimble, while the 10-gram specimens were extracted in a medium size soxhlet for 8 hours according to Federal Specification KK-L-311. The results obtained on the 10-gram specimens were considered to be the "true grease content" of the sample.

The experiment consisted of two runs, made at several weeks interval. Each run consisted of eight days of test, four for chloroform extractions, and four for petroleum ether extractions. During each day one specimen of each leather was extracted. Moreover, the four specimens extracted on a single day represented all of the four specimen sizes considered. Thus, the data for each solvent on one run constituted a Latin square (**).

In each case the extract was dried at 100°C to constant weight (±0.001 g), and the results calculated to a moisture-free basis. The results obtained are given in Table I.

*Wilson, J. A., JALCA **14**, 140-178 (1919).
†Wilson, J. A. and Merrill, H. B. Analysis of Leather McGraw-Hill Book Co., Inc., New York, 1931.
**Snedecor, G. W., Statistical Methods, Iowa State College Press, 1946.

TABLE I

Percent Grease Determined by Extraction with Chloroform and Petroleum Ether.

	Chloroform Extract				Petroleum Ether Extract			
	run 1		run 2		run 1		run 2	
Specimen Size	day	result	day	result	day	result	day	result
Chrome Tan Stuffed								
1	2	41.52	1	42.02	2	39.58	1	39.39
2	1	41.27	2	41.29	1	39.45	2	39.37
5	4	41.38	3	41.42	4	39.75	3	39.91
10	3	41.27	4	41.77	3	39.80	4	39.89
	mean	41.36		41.62	mean	39.64		39.64
Chrome Retan								
1	3	29.58	4	29.24	3	27.31	4	27.05
2	4	30.01	3	29.57	4	28.08	3	27.53
5	1	29.79	2	29.41	1	28.09	2	27.47
10	2	29.89	1	29.11	2	28.24	1	27.80
	mean	29.82		29.33	mean	27.93		27.46
Vegetable Tan Sole								
1	1	5.38	3	4.68	1	3.61	3	3.97
2	2	4.77	4	4.55	2	3.94	4	4.14
5	3	4.72	1	4.74	3	4.20	1	4.24
10	4	4.74	2	4.59	4	4.32	2	4.32
	mean	4.90		4.64	mean	4.02		4.17
Fat Liquor								
1	4	14.01	2	14.27	4	12.46	2	12.15
2	3	14.29	1	13.88	3	12.61	1	12.29
5	2	14.03	4	13.85	2	12.60	4	12.53
10	1	14.05	3	14.21	1	12.72	3	12.68
	mean	14.09		14.05	mean	12.59		12.41

A statistical analysis of the results leads to the following conclusions:

The differences observed between determinations made on different days do not, in general, exceed those between determinations run on the same day. However, for chrome retan, the results obtained in the second run by either solvent were significantly lower than those obtained in the first run. This difference is probably due to some change in the sample during the interval of several weeks separating the two runs, rather than to experimental errors.

In the case of chloroform extractions, the size of the sample subjected to the analysis, in the range of 1 to 10 grams, does not show any significant effect on the observed grease content.

On the other hand, when petroleum ether was used as a solvent, a decrease in the specimen size resulted generally in a decrease in the observed grease content. This trend, observed on all four samples, was found to be statistically significant, and was of the order of 0.5 per cent grease less for the 1-gram specimens than for the 10-gram specimens. For a given specimen size, however, the precision of the determination was found to be greater for the pe-

troleum ether extractions than for those using chloroform, the standard deviation being 0.12 per cent grease when using petroleum ether, and 0.21 per cent when using chloroform.

An examination of the petroleum ether available at this Bureau showed that approximately 3 per cent distilled over between 27 and 40 degrees C, approximately 40 per cent distilled over between 40 and 44 degrees C, and the remainder distilled over between 44 and 57 degrees C. When 60 ml of solvent is used in the extraction flask, 26 ml, which is approximately the amount needed to fill the siphon cup containing the thimble and leather, will distill under 44°C. Thus it is evident that only the material boiling below 44°C takes part in the extraction.

The low results obtained with petroleum ether when small specimens are extracted are probably due to losses incurred during the time the solvent is being removed, or during the drying process. A few simple calculations based on the data given in Table 1 and the assumption that the results for the 10 gram specimens are correct, show that when petroleum ether was used, the amount of grease recovered in each case averaged about 6 mg less than the expected value. Thus the effect would be more pronounced on small specimens. However, with chloroform, the amount of grease recovered varied by ± 4 mg. around the expected value. Of the 12 cases in the table that were considered, 5 were above the expected value, and 6 were below.

In order to determine which steps in the procedure might be responsible for the constant losses encountered when petroleum ether was used, several experiments were made using Sample 1.

The effect of temperature on drying the extract was determined by removing the petroleum ether with air jets without the aid of external heat, and drying the extract to constant weight (±0.001 g) in a vacuum desiccator. Solvent was then added in order to simulate a new determination, the removal process repeated, but the extract was dried to constant weight in a circulating air oven at 100°C. A comparison of the results obtained by drying in vacuum with those obtained by drying at 100°C showed that the loss due to drying at 100°C was less than 0.1 per cent.

The effect of prolonged heating on the steam bath was determined in another experiment. In this case the solvent was removed with the aid of a steam-bath and air jets, but the flasks were allowed to remain on the steam bath for 15 minutes after the solvent had evaporated. The extracts were then dried at 100°C in an oven, cooled, and weighed. The grease content of the 1-gram specimens was approximately 1 per cent less than the accepted value, and that of the 5-gram specimens was approximately 0.4 per cent less than the accepted value.

The effect of the presence of water on the removal of the solvent was determined in another experiment. Both petroleum ether and chloroform extracts from 1-gram specimens were used. The solvent was removed by the

use of air jets with the aid of heat from a warm steam bath. The flasks were removed just before the last of the solvent disappeared, dried in an oven at 100°C, cooled, and weighed. The amount of grease obtained with petroleum ether was 0.2 per cent less than the expected value, and the grease obtained with the chloroform was 0.4 per cent greater than the expected value. Sixty ml of the solvent used in the extraction was then added to each flask and the flask was warmed to dissolve the grease. Two ml of water was added to each flask, the solvent was removed as before, and the flasks were dried at 100°C, cooled, and weighed. The loss due to the second treatment amounted to 0.1 per cent in the case of petroleum ether, and zero in the case of chloroform.

Thus it is evident that the largest losses are obtained when the flask containing the extract is not removed from the steam bath and air jets just before the solvent has been completely removed. It is probable that part of the aliphatic portions of the grease are volatilized along with the higher boiling portions of the petroleum ether, but the full explanation of the low values is not apparent.

These observations indicate that petroleum ether does not remove all of the extractable material, and unless extreme care is used to remove the solvent, the amount of extract obtained depends upon the size of the specimen.

V. Conclusion

Rubber extraction apparatus equipped with a metal thimble can be used to advantage to determine the grease content of leather goods. The use of this equipment reduces the time required for extraction from 8 to 2 hours. Specimens weighing 3 grams are recommended for the extraction in order to make it possible to use the same specimen for a subsequent determination. The results show that chloroform removes more grease than petroleum ether and that with the former the observed grease content does not vary with the specimen size.

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A New Approach to Beamhouse Processes*

By C. C. Kritzinger

Introduction

Before hides and skins are allowed to react with mineral or vegetable tanning agents in order to produce durable non-putrescable leather, they usually have to undergo the various processes associated with the so-called beamhouse.

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Curing always involves some form of dehydration, whether it be by salt or by exposure to sun or air or by both. The tanner therefore has to soak back the stock to bring it as closely as possible to the original state. In the next process the stock is usually subjected to liming which loosens the hair and epidermis, causes swelling of the protein substances, brings about splitting of the fibres and in general prepares the material for the subsequent processes. Deliming will cause a decrease in the alkalinity and swelling and bating affects some components of the hide or skin in such a way that certain desirable physical features of the leather can be achieved.

Among tanners and leather chemists there has been a tendency to treat soaking, liming and bating as three distinct processes which have little in common, and the literature contains many contradictory and apparently contradictory theories as to what happens in the various processes mentioned. This is probably due to the fact that one theory is often stressed by its protagonist at the expense of others which may also possess part of the truth. A typical example is the controversy which has raged over the theories of the effects of bating upon the hide or skin components. Recent work by the writer [18, 19, 20, 21, 22] on globular proteins has thrown new light on the collective beamhouse operations, and one of the purposes of this review is to point out that these numerous processes all really form a continuous process which is done in several more or less well-defined steps to facilitate handling in the tannery. This paper will also endeavor to present all relevant information on soaking and especially on liming and bating in such a way that the various facts known and theories advanced will be put in their right perspective.

The Curing Process

Curing brings about so many changes in the components of the green stock that the soaking process can only be explained and understood by taking all those changes into account.

All existing curing methods depend for their efficiency upon the fact that the proteolytic bacteria are deprived of the water so necessary for their normal development as pointed out by McLaughlin and his associates [30, 31, 32] many years ago. The most noticeable overall change occurring in stock during curing is shrinkage of the structure due to such dehydration. Apart from this important dehydration there are however several less noticeable but nevertheless imporant alterations which should briefly be summarized since they affect the subsequent processes to such an extent.

Collagen and elastin fibres shrink in all curing processes, the most marked being with sun-drying. In the latter case the fibres may become rather brittle.

Reticulin fibres will also become dehydrated and brittle, but in addition appear to be affected by sodium chloride.

The erector pili muscle shrinks and the protein may be seriously denatured, depending upon the cure. Fats and oils of the sebaceous glands, dispersed

through the corium and especially plentiful in the adipose tissue, are broken down, especially in sun-drying. In salting methods there may be some removal of surface fats and oils.

The sweatglands and veins collapse, but the arteries remain more or less intact due to their strong walls of collagen and elastin.

The globular proteins undergo the most important changes insofar as the beamhouse processes are concerned, and these changes will have to be considered in some detail.

Globular proteins may be characterized[18] as non-fibrous in nature in contrast to such proteins as collagen, elastin, keratin, reticulin and muscle protein. They are generally soluble in neutral, dilute salts solutions, in dilute acid and dilute alkali, and are easily denatured.

Denaturation is by no means restructed to the globular proteins, but they show it most markedly. Broadly, denaturation may be defined[42] as "any non-proteolytic modification of the unique structure of a native protein, giving rise to definite changes in the chemical, physical or biological properties".

Decreased solubility is often the primary change in denaturation. This change is completely or at the least partially reversible, and is of the greatest importance to the tanner who always deals with partially or fully denatured globular proteins.

Other changes brought about by denaturation are loss of biological activity, loss of crystallizing ability, increased activity of the constituent groups, changes in the molicular shape resulting in a more extended form, and greater susceptibility to enzymatic hydrolysis.

Denaturation may be brought about by physical agents such as heat, freezing, pressure, irradiation by ultraviolet light, sound waves and surface forces, or it may result through chemical agents such as electrolytes, organic solvents or organic solutes, or finally it may be due to biological reactions as occur during enzymatic hydrolysis.

For the purpose of this paper we shall apply the term soluble proteins to include not only the globular proteins characterised above, but also all soluble breakdown products or building stones of proteins.

The soluble proteins form roughly ten per cent of the total protein matter in hide[19, 22]. In the corium major the largest portion is spread thinly and more or less uniformly around the fibres and fibre bundles in the interfibrillar lymph spaces[19]. The blood contains relatively large amounts as soluble serium proteins, haemoglobin, breakdown products or building stones. Finally, the fibroblasts contain mostly soluble protein material and are closely associated with the globular proteins[19].

The corium minor constitutes only 1/6 to 1/4 of the total hide thickness but it contains roughly 70 per cent. of the total soluble protein material[22] in the hide. Here again large amounts are present in the interfibrillar spaces,

in the blood and in the fibroblasts. The larger portion is, however, present as a dense layer in and immediately below the germinating layer of the epidermis [19]. This layer is the seat of cell formation for the epidermis and here the soluble proteins undergo a change to produce the fibrous keratin. In its early stages of formation epidermis keratin may then be soluble in, say, dilute saline solutions. The same must be true of the hair keratin being formed at the base of the hair root. Furthermore, the epidermis surrounds the hair follicle, even at the hair root.

How are the soluble proteins now affected by curing? In the simplest case, sun- or shade-drying, the proteins become insoluble and denatured and in extreme cases of drying and heating will be completely coagulated. This final change is not easily, if at all, reversible and is part of the reason for the difficulty experienced in soaking back such stock.

In brining and wet-salting the brine has to enter mostly from the flesh side since the epidermis is very nearly impervious. Water will flow from inside the hide to dilute the concentrated brine on the outside and vice versa. With the outward flow of dilute brines some small soluble protein particles will be removed, but as the brine inside the hide becomes more saturated the larger protein particles are gradually salted out [22] and denatured. Such proteins tend to block the interfibrillar spaces, so that proteins moving towards the flesh from the corium minor side are also precipitated when they reach this region of concentrated brine. This change is only partially reversible when the brine is diluted in soaking.

Dry-salting will combine the effects of wet-salting with some of the effects of sun-drying but the salt seems to prevent excessive denaturation by the heat.

The Soaking Process

The first process in the beamhouse appears to be the best understood and it will only be necessary to present the mass of information available in a logical and summarized manner.

The principles of soaking were thoroughly investigated by McLaughlin and his collaborators at Cincinnati [33, 34, 35, 36, 37] who pointed out that soaking is largely a reversal of the curing process: the dehydrated stock is allowed to rehydrate and the curing salt (if present) is removed.

Rehydration of the hide structure is closely related to the condition of the interfibrillar globular proteins. McLaughlin and Theis [33] showed in 1923 that the degree of rehydration is inversely proportional to the degree of dehydration occurring during curing. Kaye and Jordan Lloyd [11] indicated that excessive denaturation of the globular proteins cements the fibres together in such a way that they cannot swell properly in the soak. Recent studies by Pankhurst [46] substantiated and elaborated this work. It would seem that under certain conditions of curing (e. g. high temperature and high relative humidity) there are changes in the collagen fibres which prevent their thorough

rehydration and swelling[45], but it is probable that the difficulty in hides and skins is mostly due to irreversible changes in the globular interfibrillar proteins.

Kaye and Jordan Lloyd[11] appear to have been the first to study soaking specifically from the point of view of the desirability of removing the cementing substances. A patent was granted to them, covering the use of such compounds as sodium citrate, sodium pyrophosphate and sodium ferrocyanide as additives to the soak liquor. McLaughlin and his co-workers had found that better soaking could be obtained when dilute sodium chloride solutions were used and Pleass[47] and Dempsey[8] concluded that this was due to the better removal of interfibrillar proteins by such dilute brines. They substantiated the work of their colleagues[11] but also showed that sodium chloride, sodium nitrate, potassium perchlorate and several other salts could be used effectively.

In more recent studies along these lines Roddy and his associates[44, 50, 51] showed again that the use of a 10 per cent sodium chloride soak resulted in production of better leather and that polyvalent salts have a strong dispersing action on globular proteins. Sodium polysulfide was also found to be useful, an observation substantiated by other workers[55]. Recent unpublished work by the writer[23] has shown that sodium fluosilicate can be used advantageously in the soaking of all types of cured stock.

One aspect of soaking still requires to be mentioned. During soaking the water will penetrate almost exclusively from the flesh side, diluting the concentrated brine inside the salted hide and setting up a concentration gradient which is the reverse of that obtaining during curing. Some of the partially denatured globular proteins now redissolve in the dilute brine and are removed. Once again then it is the corium major which is being stripped of globular proteins whilst the more readily soluble portion only is extracted from the corium minor[22] during the relatively short soak. In this condition the stock now enters the next process.

The Unhairing Process

The use of slaked lime for loosening of the hair in the tannery is probably several thousand years old, the main improvement in the process being the use of reducing agents such as sodium sulfide to assist the natural hair-loosening action of the lime liquor. Especially during the past twenty or thirty years much attention has been given to the breakdown of the cystine link by alkaline reducing agents, perhaps to the detriment of a better understanding of the other factors involved. The present accepted concept of the liming process can be summarised briefly in the following paragraphs.

The main aim of liming is loosening of the epidermis and hair to facilitate their removal in the mechanical unhairing operation. The theory of this action, which has received almost exclusive attention during recent years, is that the cystine di-sulfide bridge in the keratin molecule is broken by the

alkali and is prevented from reforming by reducing agents. This aspect of the liming process has been reviewed in full recently by McLaughlin and Theis [40] and Bowes [4].

A second important function of liming is to complete the rehydration started by soaking. Full details of this subject will also be found in the work mentioned.

Liming is responsible for the removal of a large portion of the remaining soluble proteins, thereby opening up the interfibrillar spaces. The lime can then enter more easily and will break down the reticulin sheaths which bind the fibres together. Fibre-splitting can now occur as a function of globular protein removal and reticulin breakdown [19, 40].

Some saponification and removal of surface fats takes place, but the lipids in the corium are affected only to a minimum, if at all [13, 14, 15, 16].

It would seem that this theory errs in putting too much emphasis on the breakdown of keratin as the principal cause of hairloosening. There are many depilation processes or agents which do not involve any keratolytic action.

In the simplest case it is well-known that when green hides are allowed to putrefy the hair and epidermis can be removed quite easily. Hairslip on brined or wet-salted stock is a common phenomenon. In both these cases the loosening is due to the enzymes secreted by proteolytic bacteria, and the industry of wool-pulling by the sweating process depends upon this very phenomenon. Furthermore, some enzyme preparations for hairloosening are commercially available.

Immersion of the fresh hide or skin for about 10 minutes in water at 60°C will loosen the hair and epidermis [5, 43]. Dehairing of hogs and pigs by scalding is, of course, common practice and resin preparations are now marketed which are used along the same lines. It is interesting to note that too high temperatures or excessive immersion will defeat the object, since the hair and epidermis will then stick.

In 1906 Stiasny [54] reported that ammonia in the lime liquor will increase the rate of unhairing, and will cause unhairing also when used along. Ross [53] also obtained unhairing of fresh hide with ammonia and recently Lennox and his associates [26] made a detailed study of the effect of ammonia in the pulling of wool. These workers also showed that various amines will increase the rate of wool-loosening. The "sharpening" effect of amines in lime liquors has, or course, been known since the studies of McLaughlin and his associates [38] in 1927 and is used commercially.

Marriott [27] employed acetic acid to obtain unhairing and actually produced leather from stock treated in this manner. He suggested that hydrolytic action of the acid on a protein similar to mucoid was responsible for the loosening. Ross [53] obtained unhairing with hydrochloric acid.

Solutions of 5 and 10 per cent sodium chloride have been found to give satisfactory loosening of the epidermis and hair in fresh hides within a few days, with or without changes of the solution [5, 21, 22, 43].

Gustavson[10] recently again showed that fresh hide could be unhaired in three to five days with concentrated solutions of urea.

Saturated (0.6 per cent) solutions of sodium fluosilicate were found by Kritzinger[17] to give loosening of the hair and epidermis in fresh hide and in a recent private communication Mr. R. Beakbane disclosed that he has since made similar observations.

In most of the cases cited fresh hide or skin had been employed but Kritzinger[23] has recently found that cattle hides, calfskins, goatskins and sheepskins which have been wet-salted, dry-salted or sun-dried can be unhaired with saturated sodium fluosilicate solutions at room temperature in 6 to 14 days, depending upon the type of stock and the curing method. The entire epidermis comes off in sheets, bringing away the hairs and hair follicle walls.

In view of the various observations is has become clear in recent years that the loosening of the epidermis and hair is not only a function of the breakdown of keratin by reducing alkaline solutions, but that the soluble proteins of the corium minor play an important part too. Ross[53] in 1924 appears to have been the first to realize the importance of these cementing substances in the unhairing processes. Ross concluded that such unhairing as he obtained in fresh sterile hides was due to autolytic action which "digests the albuminous substance connecting the epidermis with the grain" in such a manner that the epidermis with its hair could be removed in intact sheets of several square inches.

Of several other later references to the possibility of the globular proteins being involved in the process of loosening the epidermis and hair two recent (1948 and 1949) papers by Kritzinger[21] and Gustavson[10] appear to have put the subject most clearly. The former suggested "that the present theory of unhairing by lime liquors does not give the complete picture, and that the removal of the globular proteins in the native or denatured state might be of much more importance than has been realized" Taking note of this remark Gustavson compares the unhairing obtained by urea with that by sodium chloride and states that such unhairing is "probably due to the dispersing and modifying action of these lyotropic agents on soft keratin and other z-proteins of the mucous layer, which in many respects show similarity to the globular proteins." Gustavson also draws attention to observations that the keratin of the lower layers of the epidermis contains less sulfur than the hair and is in a "young" state. More recent work by Buechler and Lollar[5, 6] has shown that the epidermis should perhaps "be considered as a tissue containing a mixture of proteins, one of which may be keratin existing only to a small amount."

We may therefore think of the epidermis and hair as being embedded in and cemented to the corium minor by a dense layer of soluble proteins. Loosening of these structures must then occur if the soluble proteins are removed or affected in such a way that they no longer cement the epidermis and hair to the underlying tissues.

In cases of enzymatic unhairing (autolysis, putrefaction of green or cured stock, sweating, etc.) the enzymes break down the globular and other soluble proteins such as young keratin to such an extent that they no longer have the ability to cement the epidermal structures to the tissues underneath. At this stage it might perhaps be mentioned that the soluble proteins are more subject to breakdowns by bacteria. Unhairing by hot water is also due to a change in the soluble proteins as a result of thermal agitation. If the treatment is prolonged or the temperature too high then coagulation will result and the epidermis and hair will adhere to the corium minor even more rigidly. This also appears to be the explanation of the difficulty encountered in unhairing flint-dried stock. Unhairing by sodium chloride has up till now only been found possible on fresh stock, where no denaturation has occurred. In salted or dried stock the denaturation is only partially reversible in dilute salt solutions, hence hairloosening cannot be achieved. Sodium fluosilicate has such a strongly dispersive action on even denatured globular proteins that fully cured hides and skins may be unhaired with relative ease. In this case, however, salted stock should be well soaked and washed first to remove sodium chloride which would otherwise salt out the sodium fluosilicate from a saturated solution.

On the basis of this approach any lyotropic or hydrotropic which can disperse native or denatured globular proteins should act as an unhairing agent. This also seems to be the reason for the action of urea [10] and of the amines.

Lime unhairing presents a special case now. During the initial stages of liming a portion of the globular and other soluble proteins will be removed from the corium through the flesh side. Meanwhile the keratin is being broken down and dissolved, as postulated before, thereby making the epidermis so porous and loose that the soluble proteins adjoining it can be removed with ease. Before such removal is complete, however, the stock is unhaired in normal practice so that a large amount of globular proteins and soluble breakdown products of proteins is carried forward into the subsequent processes.

The Deliming Process

Where lime unhairing has been used it is necessary in most cases to delime the stock afterwards by using acids. This decreases the excessive swelling, removes some or all of the lime, and removes a certain amount of surface fats and soluble protein material.

The Bating Process

It seems reasonably safe to attribute the fallen condition of bated stock mostly to the removal of lime and the dressed swelling (hydration) by means of acids during deliming or acid salts used in conjunction with bating. Similarly the rubbery feeling can be removed almost entirely by deliming but the stock will not be flaccid, smooth and slippery.

No amount of ordinary deliming will produce stock through which air and water can be squeezed or which will produce soft leather. What then does bating do to limed material?

In the earlier studies of the bating process it was thought that the changes brought about in the stock were due to effects of the bate on the collagen. Thomas and Seymour-Jones[56] thought that considerable digestion of collagen occurred by pancreatic bates, but Marriott[29] stated that their experiments had been done on hide powder, i. e. denatured collagen, and could not be considered. Merrill and Fleming[41] found that limed and fresh collagen were affected by trypsin but that very little attack occurred during practical bating. In 1934 Bergmann[3], however, proved that collagen was not affected by tryptic enzymes. Marriott's suggestion[29] that bating removes what he terms β-collagen formed during liming seems to have been disproved by Anderson[1].

Küntzel[24] advanced the idea that bating alone could remove the hysteresis caused by liming. Anderson[1] thought that he had proved this idea erroneous, but there is some doubt as to the validity of his experimental procedures and the conclusions based thereon. By measuring thickness and weight effects Cunningham and Shuttleworth[7] have shown that bating does remove such hysteresis while deliming with ammonium chloride does not. What effect, if any, this has on the quality of the finished stock still remains to be clarified.

Tannery experience shows that flesh splits are only negligibly affected, if at all, by bating but that grain splits are affected most markedly. Since the elastic tissue is concentrated in the corium minor, it was thought by Rosenthal[52] and Wilson[58, 59] that bating digests elastin. Marriott[28, 29] could not find any such breakdown and Wilson also later abandoned that theory.

McLaughlin and co-workers[39] thought that bating affected the reticular tissue, but extensive studies by Kaye[12] and Roddy and O'Flaherty[48] have shown this not to be the case.

During scudding after bating considerable amounts of pigments and hairroots are loosened. It was therefore suggested by Wilson and Merrill[60] that bating removes the keratoses (i. e. keratinous breakdown products). This theory was disproved by McLaughlin and his associates[30] and recently by Anderson[1]. The removal of hairroots after bating is probably made possible by the decreased swelling whereby the hair follicles are opened again to make removal of such debris mechanically possible.

Commercial pancreatic preparations contain rennase to a greater or less degree. Lenk[25] therefore suggested that bating was typical rennase action[1] whereby the fibres are coagulated and shrunken, thus allowing for moisture to be squeezed through the stock and bringing about the fallen condition. Anderson[1] could disprove the theory conclusively.

Bating preparations contain lipolytic enzymes and some removal of fats is therefore to be expected. Moreover, the warm bath will wash out some of

the lipids and to a certain extent their presence on the surface might account for the slippery feel of bated stock.

Only changes in the erector pili muscle and the remaining globular and other soluble proteins can therefore account for the softness and porosity of the stock and the smoothness of the grain.

It is well-known but not always fully appreciated that the involuntary erector pili muscles are still quite active even after normal bating. If a skin from a light but warm bate is dumped in cold water there is sure to be a contraction of these muscles to give rise to gooseflesh. If the stock is tanned in this state, then the grain is bound to be rough and coarse. Similarly, stock from the cold lime liquors and deliming bath will show coarse grain due to the gooseflesh. Recent work by Anderson [2] has shown that bating affects the muscles and breaks down the protein, as well as eliminating gooseflesh by the warm treatment. The smoothness of the grain in bated stock is therefore largely a function of the breakdown of these muscles. But at the same time it is also due to the bate smoothing out the different degrees of swelling in the various fibrous structures.

To a large extent porosity and softness of the stock can be achieved merely by deliming to decrease the swelling, but the normal porosity and softness of bated stock is probably largely due to removal of the interfibrillar proteins. Eitner [9] suggested as long ago as 1911 that bating removes such proteins, and his observation was accepted by Marriott [28] and Turley [57]. Kaye and Jordan Lloyd [11] provided experimental proof for this theory and McLaughlin and his colleagues [39] considered the removal of interfibrillar proteins by tryptic enzymes to be the principal function of bating. Anderson [1] first stated that removal of these proteins did not affect the quality of the stock at all, but later [2] suggested that their removal might perhaps be an essential preliminary for proper action of the bate on the erector pili muscle.

Ross [53] thought that the pieces of hide which he had unhaired with autolysis and with sodium salicylate appeared to be bated. Kritzinger [17] reported that fresh hide from which the epidermis and hair had been stripped in eight days with sodium fluosilicate lost "its characteristic pliable and elastic feel, giving it the appearance of a bated hide". More recently [22] it has been found with larger numbers of hides as well as skins (three to six in each experiment) that it was difficult to tell bated from fluosilicate stock. Chrome leathers have been produced using the "sodium fluosilicate beamhouse" which are at the least comparable to conventional leathers. The grain, in particular, was very smooth and tight in those leathers. This proves that the action of a sodium fluosilicate beamhouse is similar to the combined action of normal liming, deliming and bating.

It can therefore be stated that the functions of the normal bating operation are:

1. Deliming and decreasing of the alkaline swelling whereby the differences between the various structures are smoothed out.
2. Opening up of the structure so that water and air may pass through freely by removal of the interfibrillar proteins which remain especially in the corium minor despite the previous processes.
3. Breakdown of the erector pili muscle and adjustment of this muscle to a higher temperature, whereby a smoother grain is assured.

Conclusion and Summary

Although the beamhouse operations are normally done in several steps (soaking, unhairing, bating) they are dependent upon one another and in fact form a continuous process. The common denominator for these processes is the globular and other soluble proteins, since at least one of the various aims of each process is the removal of these materials. In the same way the practice of varying the different beamhouse processes to suit the type of curing given to the stock is due, amongst others, to the different ways in which the globular proteins react to different curing procedures.

Soaking is largely a reversal of the curing process, i. e., the salt (when present) is removed and the stock is allowed to rehydrate to approximately the same degree obtaining before dehydration was brought about by curing. The ease and degree of rehydration are dependent upon the extent of denaturation brought about by curing in the various fibrous and globular proteins. The beneficial effect of such soaking aids as sodium chloride, polyvalent salts, etc. is the result of their efficiency in despersing and removing interfibrillar proteins which would otherwise cement the fibres together and prevent their thorough rehydration.

Loosening of the hair and epidermis is primarily a function of the removal of the layer of soluble proteins cementing these structures to the corium minor, or of such a change in these proteins that they lose their cementing power. It is possible that alterations in and removal of the proteins may occur together. That depilation is controlled by these factors is evidenced by the fact that it can be brought about, without involving breakdown of the keratin in the epidermis, by such agents as controlled temperature, enzymes from various sources, sodium chloride, sodium salicylate, sodium fluosilicate, acetic acid, hydrochloric acid, ammonia, urea, etc. In general it would seem that any lyotropic or hydrotropic agent which can disperse native or denatured globular proteins should be a good depilation agent. Depilation by straight lime or lime containing reducing agents of the sulfide type also depends primarily upon removal of and attack on the soluble proteins, but breaking of the disulfide cystine link in the keratin aids such removal. Although disintegration of the relatively impervious epidermis in lime liquors allows extraction of the interfibrillar proteins also from the grain side, the stock is usually unhaired mechanically before the extraction is complete. In non-keratolytic processes the proteins have to be removed almost exclusively from the flesh

side, and by the time loosening of the epidermis sets in the interfibrillar substances have been removed to a large extent.

Liming continues the rehydration of the stock started in the soak, saponifies some of the surface lipids, and brings about fibre-splitting as a function of breakdown of the reticulin sheaths.

The softness and porosity of normal bated stock seems to be mostly a function of the removal of interfibrillar proteins remaining after soaking and liming. The characteristic smoothness of the grain of bated stock is a result of breakdown of the erector pili muscle, but in addition the bate smoothes out the differences in the degree of swelling, brought about by liming in the various fibrous structures, by decreasing the degree of hydration.

Acknowledgment

The work which has led to the ideas advanced in this paper was started at the Tanners' Council Laboratory, University of Cincinnati, under Drs. Fred O'Flaherty and Wm. T. Roddy, to whom the writer wishes to extend his sincere appreciation for their generous guidance, assistance and constructive criticism.

Thanks are also due to my colleagues on the staff of this Institute for their helpful interest in this work.

Leather Industries Research Institute,
Grahamstown, South Africa.
September 15th, 1950.

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A Method for Measuring Puncture Resistance of Leather and other Materials

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ABSTRACT

As a method of evaluating the protection afforded the foot by a shoe sole, a new test has been devised which measures the resistance of shoe materials to penetration by sharp objects. This can be attached to a Scott tensile tester or other similar machines.

INTRODUCTION

The puncture resistance of shoe bottoms is of real importance to the parents of children and to persons who may work where such hazards exist.

The resistance of any material to puncture is also related to the comfort of the wearer of a shoe. A shoe sole which offers little resistance to a nail or other sharp objects penetrating it would fail to provide comfort when one walks over a rough surface such as loose gravel or cinders.

A nail puncture can result in serious infection. Similar injuries can also occur from such things as glass, wires, and even rakes or pitchforks.

As a means of evaluating this property of shoe soling materials we have developed a test method. Using a standard horizontal Scott tester we have modified it by the addition of a device which punctures the material with a nail.

APPARATUS

The device is made of cold rolled steel though other materials would serve as well. It fastens to the Scott tester in place of the jaws and consists of the following parts all welded into a unit structure:

1. Two plates 3½ by 5 by ¼ inches, pierced in the center by a ¾ inch hole for bolting to the Scott tester.
2. Two rods 1 by ½ by 13 inches, welded to one of the above plates on opposite sides and parallel to each other perpendicular to the plate. Space between rods 3½ inches.
3. One plate 3½ by 4 inches welded to the other end of these rods.
4. One cylindrical block with a .010 hole through the center in which a 6 penny nail can be inserted and clamped by an allen head screw. This is welded in the center of the last plate so that the nail is on the center line with the point toward the jaw. Block dimensions 2 inches diameter by 1½ inches high.

5. Four rods ½ by ½ by 13 inches which are welded perpendicular to the second of the 3½ by 5 plates in the form of a rectangle ½ inch apart and 4 inches apart so the 1 by ½ rods slip easily between them.
6. One plate 3½ by 5 inches with a ½ inch hole drilled in the center and notched ½ by 1 inch deep in the center of the 3½ inch edges. This is placed in between the ½ by 1 rods and the four rod section threaded over and welded to this plate. The parts should slide easily on each other so the nail goes through the hole.
7. A stripper plate is added ½ inch toward the nail block from plate 6 and fastened to rods 5. This has a ½ inch hole in the center and acts to pull the nail from the specimen when the machine is reversed.

Figure 1 shows a diagram of this device as assembled.

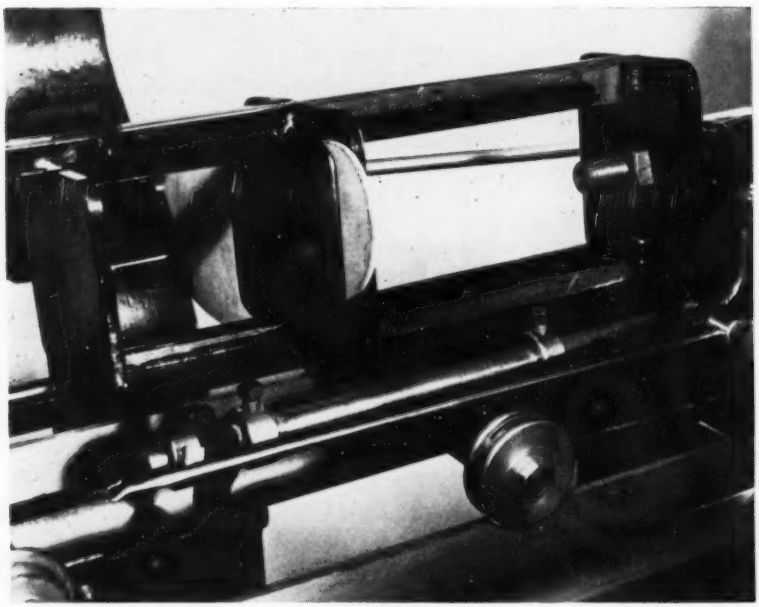

FIGURE 1.

This is a modification of a similar device made by Mr. Frank Marshall of Keystone Tanning and Glue Company.

Procedure

Thickness is measured as in the A.L.C.A. Methods of Sampling and Analysis, Method E-16, over the area to be punctured. The material to be tested

is placed between the base plate and the stripper plate and the machine operated until the nail penetrates through the specimen. On reversing the machine the nail is pulled from the specimen by the stripper plate. The puncture resistance is recorded just as in any other strength measurement and may be reported in pounds or pounds per inch thickness as specified.

Experiments and Discussion

Using this apparatus a series of 7 leather samples and 7 substitute soling materials were tested. The sole leathers were selected as being representative of all qualities available and a special effort was made to include the poorer as well as the better grades. The substitutes were for the most part purchased on the open market and representative of materials used for resoling shoes; some were acquired from shoe manufacturers.

In an attempt to ascertain the effect of the sharpness of the nail point on the value obtained a series of representative samples were measured using 6 penny nails of various degrees of sharpness with both conical and pyramidal points. Little difference could be noticed with nails of the same angle of sharpness, though with a nail with the point cut off flat, values from 30 to 40 lbs. higher were recorded. The first value obtained with any sample varied somewhat from the mean value which was probably due to the wax or oil left on the nail from the previous specimen. Considerable variation was noticed over the area of both the leather and the synthetics though little variation (5 per cent) was noticed for adjacent punctures. Some of these data are shown in Table I.

TABLE I

Puncture Resistance of Soling Materials

Substance		Thickness Inches	Puncture*	
			Lb.	Lb./in.
Vegetable Sole	A	.217	94	434
	B	.230	125	543
	C	.240	116	484
	D	.202	144	713
	E	.235	244	1040
Vegetable Chrome Sole		.224	136	613
Chrome Vegetable Sole		.260	104	400
Synthetic Sole	A-1	.250	67	268
	A-2	.260	55	211
	B-1	.255	58	228
	B-2	.255	46	180
C Cork Rubber		.310	37	119
C Rubber		.250	41	164
B Composition		.325	42	129
B Rubber		.351	43	122
Neoprene Crepe		.360	26	72

*These are the average figures for ten determinations using a 6 penny finishing nail, .092 inches diameter.

A further test was made to note the effect of decreasing the size of the nail used to puncture the specimen. A nail of .079 inches diameter was substituted for the .092 inch 6 penny nail. Some of these data are given in Table II.

TABLE II

A Comparison of the Puncture Resistance of Soling Materials Determined Using Nails of Different Diameters

Material	Puncture Resistance Pounds per Inch		Ratio
	0.92" Nail	.790" Nail	
Vegetable SoleB	543	465	1.17
Vegetable Sole E	1040	850	1.22
Synthetic B-1	228	204	1.12
Synthetic A-1	268	214	1.25
B Rubber	122	108	1.13
Ratio of the diameters of the two nails			1.18

The determination of resistance to nail penetration could be an important addition to the physical testing of leather. The variables of thickness, extent of rolling, wear, aging, flexing, and other factors on the resistance of leather to puncture can make an interesting study.

Received August 10, 1950.

Studies on Shoe Fillers

By Joseph R. Kanagy

National Bureau of Standards

I. Introduction

Shoe fillers are used in the manufacture of welt shoes to fill the space, typical of this type of construction, between the innersole and the mid, slip or outersole. When the welt is attached to the channeled lip of the innersole and the lasting edge of the upper, a ridge is formed around the shoe bottom where the upper meets the attaching sole. To build up the void space even with the ridge and form a flat surface on which to fit the sole, shoe fillers are applied. These materials are usually put in place by hand with a spatula. A slight amount of pressure is used to pack down the filler and to form a smooth surface.

The characteristics of these materials must include properties which permit application in a soft pliable form. Furthermore, the materials should set and stiffen to form a firm foundation. Two types of materials are used; both consist principally of ground cork incorporating a binder. One type contains

a thermoplastic binder that softens on heating, and which after application resets stiff; the other has the binder in a solvent, which on evaporation leaves a material which sets and becomes stiff.

All specifications for these materials are based on a chemical analysis to determine the percentage of binders and cork. These analyses are difficult to perform accurately, since many complications arise between the extracting solvents and the binders. Some binders are much more difficult to remove from the cork than others. The ratio of binder to cork, even if determined accurately, gives little information with regard to the service characteristics of the fillers. Since the fillers in the shoe bottoms are subjected to repeated loading and unloading, and their flow properties appear to be highly important, it was believed that a more useful test to apply might be developed from indentation and recovery measurements.

II. Procedure

Since the fillers are placed on the shoe bottoms, spread out and compressed by means of a spatula, a method simulating this treatment was chosen to prepare the materials for the indentation and recovery tests. Samples of the fillers were placed in a press and compressed under a load of 5000 pounds over an area of about 25 square inches to form a flat disk. For the samples containing solvent, a slight modification was made in the method used for forming the disks. The disks were formed by a preliminary pressing under low pressure. A drying period of 24 hours at room temperature was then allowed for the elimination of volatile material before the final pressing was made. The pressure applied to form these disks is probably greater than that applied in actual practice, but the procedure permits the evaluation of the materials on a comparative basis.

Indentation and recovery tests were made on the disks at 73°F and 90°F, with the apparatus described in report BMS 14 by P. A. Sigler and Myrtle B. Woodward. A 0.5 square inch indenter (approximately 0.8 inch diameter) was substituted for the ¼ inch in diameter indenter. The indenting was done under a load of 20.2 pounds. Recovery was determined under no load in the indentation apparatus immediately after the indentation period.

Determinations of the densities of the pressed materials were made on a circular disk about 2¾ inches in diameter, cut with a die. From the dimensions of the disks and their weights, the apparent densities were calculated.

The amount of binder in the fillers was determined by extracting with benzene, and the amount of solvent by heating the filler in an oven at 100°C for 24 hours.

Tests were made on seven different samples, obtained from two companies, A and B. The former supplied one thermoplastic and four of the solvent type, the latter supplied one of each type.

III. Results and Discussion

The results for indentation of the pressed fillers under a load of 20.2 pounds, on a 0.5 square inch in area presser foot, for a period of 10 minutes, and those for the recovery of the fillers under no load for a similar time period are given in Figures 1 to 7. Results obtained at 73°F are compared with those obtained at 90°F.

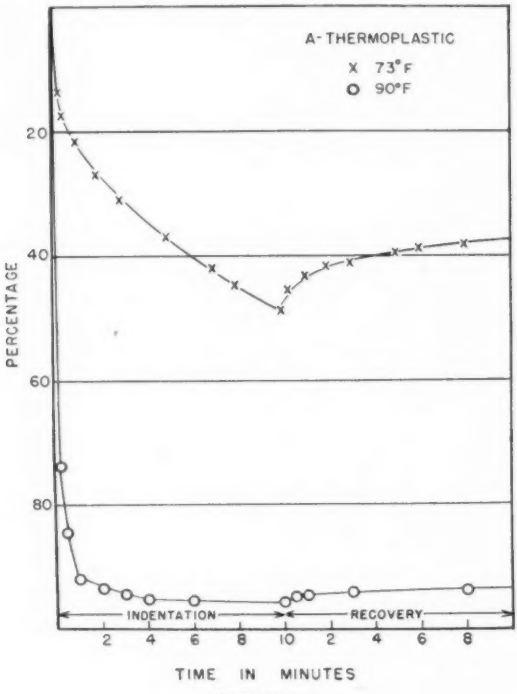

FIGURE 1.

All of the samples show greater indentations at 90°F. than at 73°F. The thermoplastic materials, however, show much greater increases in indentation with increase in temperature than do the solvent type fillers. The solvent type fillers show the greater amounts of recovery at both temperatures. For the thermoplastic fillers there is practically no recovery at 90°F because they are penetrated by the presser foot almost completely.

The effect of various binder and cork composition combinations is demonstrated by comparing the behavior of solvent types A-1, A-2, and A-3. A-3 is composed of the cork in A-1 and the binder in A-2. It is to be noted that its indentation properties are different from either A-1 or A-2.

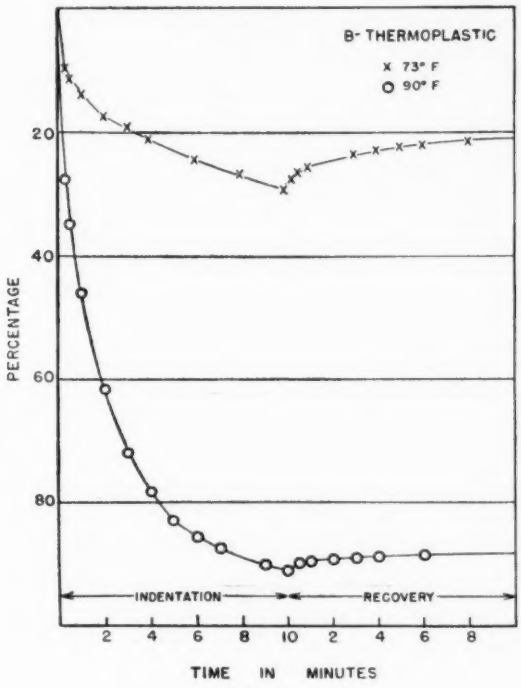

FIGURE 2.

TABLE I

Results of Indentation and Recovery Tests on Shoe Fillers

Manufacturer	Type	Density g/cm³	Indentation		Recovery	
			73°F. Per Cent	90°F. Per Cent	73°F. Per Cent	90°F. Per Cent
A	Thermoplastic	0.565	48.7	95.7	11.3	1.7
B	"	0.702	28.7	91.0	7.8	2.6
A-1	Solvent type	0.288	45.7	53.9	27.2	31.7
A-2	" "	0.425	25.6	40.3	18.9	27.7
A-3	" "	0.482	14.4	31.6	10.6	22.2
A-4	" "	0.434	18.8	35.0	16.0	24.5
B-1	" "	0.364	46.8	58.0	27.5	35.9

The results of the indentation and recoveries of the fillers, together with their densities, are tabulated in Table I. Indentation and recovery are in percentages of the total thickness of the sample. It should be noted that

TABLE II

Solvent and Binder Composition in the Shoe Fillers

Filler	Solvent Per Cent	Binder Per Cent
A — Theremoplastic	——	79.6
B — "	——	75.9
A-1— Solvent type	58.3	25.7*
A-2— " "	25.1	29.1*
A-3— " "	24.6	24.4*
A-4— " "	35.0	26.9*
B-1— " "	60.5	68.9*

*Results calculated on solvent-free basis.

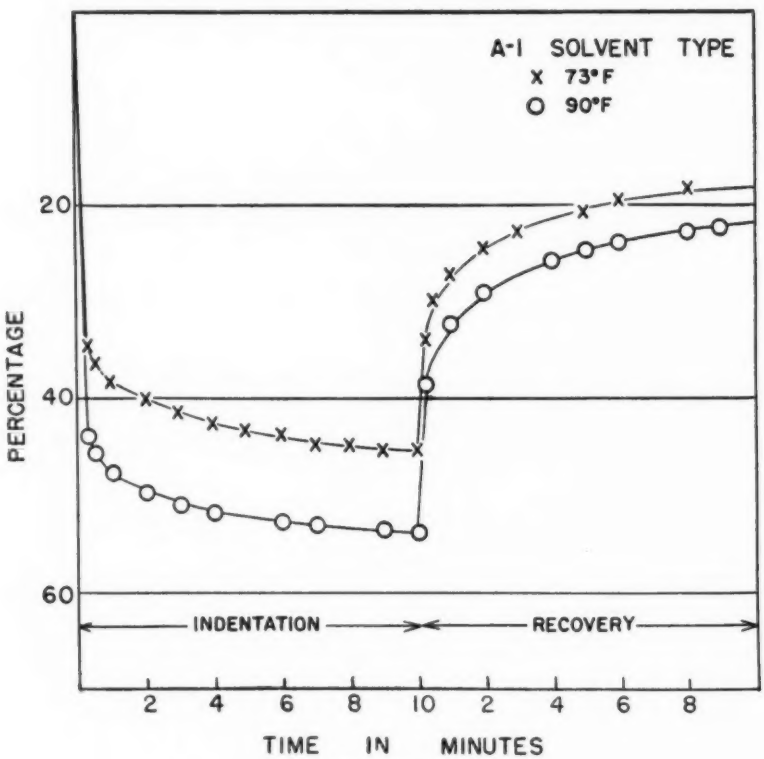

FIGURE 3.

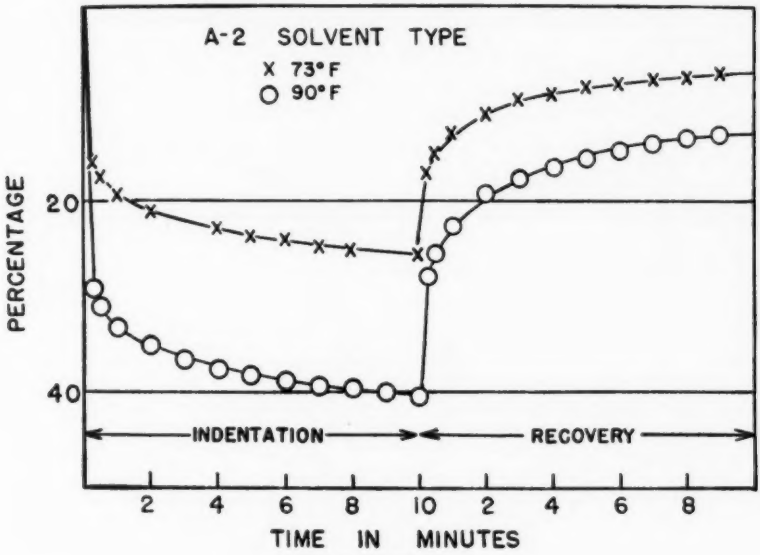

FIGURE 4.

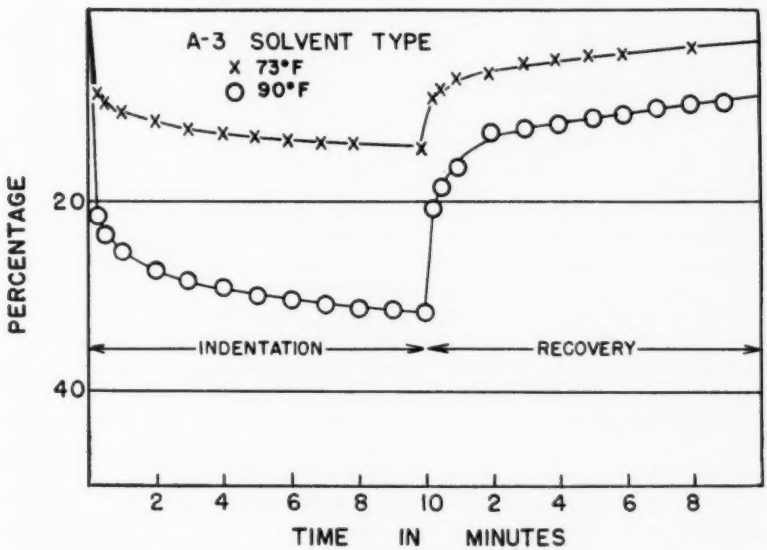

FIGURE 5.

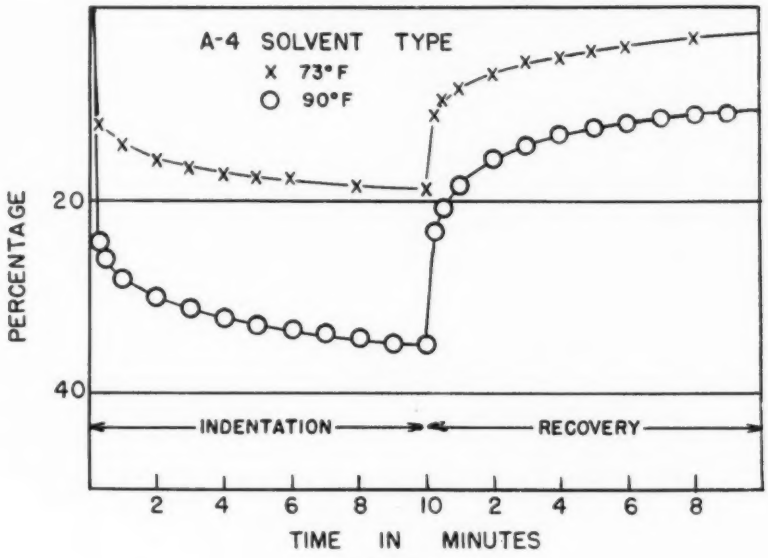

FIGURE 6.

there is a definite correlation between the density of the material and the indentation value, if separate comparisons are made among the thermoplastic materials on the one hand and the A solvent types on the other. It appears from this, that when similar binders are present in approximately the same percentages the indentation is proportional to the density of packing. Therefore, the density might be used as a criterion for evaluating the fillers.

The percentages of binder in the fillers, as determined by extracting with benzene, are given in Table II. The percentages of solvent in the solvent type fillers, as determined by drying in an oven at 100°C for 24 hours., are also shown. The amount of binder in the thermoplastic fillers is comparatively high, and could probably be the reason for their low recoveries. On the other hand, the percentages of binder in the A solvent type fillers are only about half as great as that in the thermoplastic types. The properties of the solvent type fillers are therefore more closely allied with those of the cork than with those of the binders.

IV. Conclusions

From the results of these tests it appears that the solvent type material might be better for shoe fillers than the thermoplastic type. The former shows high recoveries at both 73°F and 90°F. The thermoplastic materials, on the

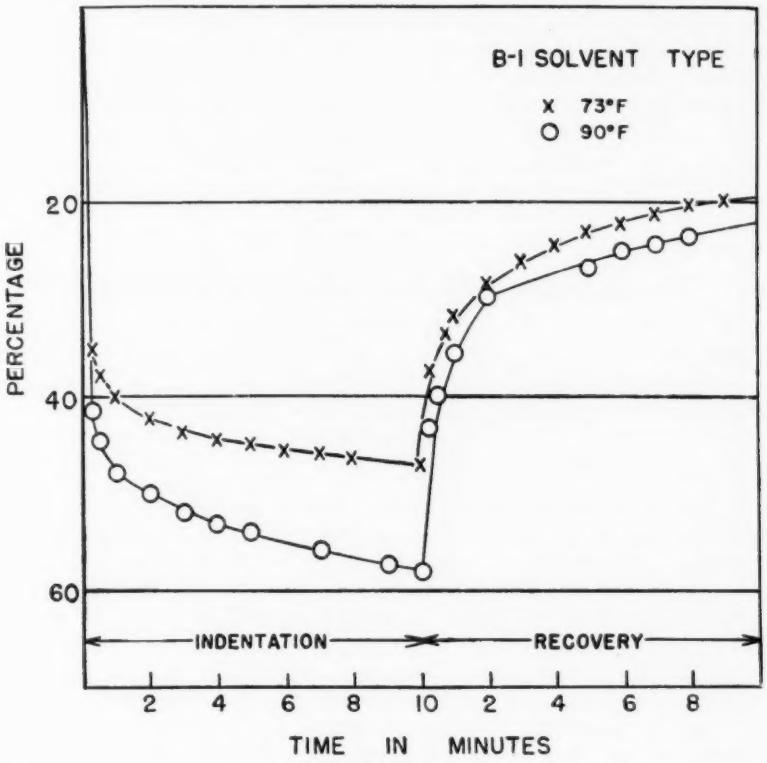

FIGURE 7.

other hand, appear to have practically no recovery at the higher temperature. This indicates that they may offer an unstable foundation for the foot, expecially since the temperature of the shoe may even exceed 90°F on hot summer days. During warm weather these materials probably will flow under pressure and the shoe bottom will not hold its shape. Consequently, low places will be formed on the shoe bottom where the foot exerts the greatest load. The opinion has been expressed that the bottom of the shoe should remain level and smooth, and consequently the flowing of the filler is believed to be one of the causes of foot discomfort.

On the basis of results obtained in this investigation, it is suggested that indentation and recovery tests be applied in the evaluation of materials for shoe fillers. Reliance on these methods instead of the chemical tests now used in specifications should eliminate some of the difficulties now encountered

in acceptance testing and should also result in the development of more suitable materials for this purpose. Actual service tests to compare the performance of the two types of fillers are definitely warranted from the results of these experiments. Efforts should also be made to determine the proper type of shoe bottoms for comfort.

Received Nov. 2, 1950

The Isolation of Hydroxyproline and Proline from Collagen*

By JOHN H. HOWARD

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Collagen has long been known to contain many of the amino acids. It is particularly rich in proline and hydroxyproline. Both of these amino acids are extensively used in microbiological assays for certain amino acids and vitamins. They also have a potential use in nutrition studies and experimental medicine. Their recovery in quantity is therefore of economic interest to the tanner, as they may represent by-products of considerable value.

Proline [1] and hydroxyproline [2] were first isolated from protein hydrolyzates by Fischer early in the current century. Since then, numerous methods have been used to isolate these amino acids. These include n-butanol extraction followed by n-propanol extraction [3], reineckate formation [4], the copper salts' method of Town [5], picrate formation with subsequent decomposition with aniline [6, 7], and rhodanilate formation [8]. The methods are generally tedious and the amino acid products, both in quantity and quality, leave much to be desired. Recent work has emphasized the use of solvent extraction, especially the patent by Sifferd [9] and the investigations of McCollum and Rider [10]. Hamilton and Ortiz [11] have recently prepared the N-nitroso derivatives of proline and hydroxyproline by treating the respective amino acids with nitrous acid. Their attempt to isolate proline and hydroxyproline from gelatin with use of the N-nitroso derivatives gave low yields.

This paper describes a new and unique method for isolating both proline and hydroxyproline from a collagen hydrolyzate.

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It represents a part of the thesis presented by John H. Howard to the Graduate School of Arts and Sciences, University of Cincinnati, in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June 1951.

Material

A salt-extracted corium split of a steer hide [12] was used as the source of a purified, native collagen for this research. Analysis of the powder showed it to contain 15.61 per cent total nitrogen, 0.50 per cent ash, 0.03 per cent lipids, 0.16 per cent total carbohydrates, 0.10 per cent pentoses, and 12.90 per cent moisture. Its amino acid content has been quantitatively determined by Neuman [13] and its purity by Jacobs [12].

Procedure

Collagen (5 grams) is hydrolyzed by refluxing for sixteen hours with 30 ml. of 6 N hydrochloric acid. The hydrolyzate, decolorized by boiling fifteen minutes with one gram of Norit-A and filtering, is further acidified with 15 ml. of concentrated hydrochloric acid, diluted with water to 270 ml., and heated to 60°C. Nitriting is accomplished at 60°C by slowly adding 90 ml. of a solution (preheated to 60°C) containing 7.2 grams of sodium nitrite. After thorough mixing, the solution is held at 60°C for ninety minutes with shaking every fifteen minutes. After simmering for one hour, most of the solvent is removed by straight distillation, finally concentrating to a slush on a steam-bath, and extracting four times with 12.5 ml. aliquots of concentrated hydrochloric acid to leach out the proline hydrochloride and hydroxyproline hydrochloride. The combined extracts are taken to dryness in vacuo, redissolved in water, residual hydrogen chloride removed with silver carbonate, residual silver ions removed with hydrogen sulfide, concentrated in vacuo, dried in vacuo at 60°C, and extracted with absolute ethanol (100 ml. for each gram of proline expected). The insoluble hydroxyproline is removed by filtration and dried in vacuo at 60°C for sixteen hours. The ethanol extract is taken to dryness in vacuo under 60°C. The white crystals of proline remain on the bottom of the dish and the gunk collects on the sides of the container.

Results

Three similar experiments were carried out using the above technique. A maximum yield of 0.335 gram of crude hydroxyproline was obtained. Neuman and Logan [14] report a value of 13.3 per cent hydroxyproline for this collagen. On the basis of this figure the above maximum yield converts to 57.8 per cent of the theoretical value. A maximum yield of 0.1058 gram of crude proline was likewise obtained. Neuman [13] reports a value of 16.5 per cent l(-) proline for this purified collagen. This yield is thus 14.7 per cent of the theoretical value.

The analyses of the crude fractions of proline and hydroxyproline obtained from these three experiments are given in Table I. Hydroxyproline was determined by a modification of the method of Neuman and Logan [14]. A Beckman spectrophotometer was employed to read per cent transmission after

color development, a wave-length of 560 millimicrons was selected since maximum absorption was found to take place there rather than at 540 millimicrons as recommended by the original investigators. l(-)Proline was determined microbiologically by the method of Dunn, et al. [15]. Total nitrogen, ash, chlorides, and ammonia nitrogen were determined by the usual microtechniques. All of the samples were dried in vacuo for sixteen hours at 60 C, weighed, dissolved in water, diluted to a specific volume, and aliquots used for the various analyses except in the case of the proline fractions. Hydroxyproline was determined in the proline fractions with use of a separately weighed, dry portion of each sample.

TABLE I

Analyses* of Crude Fractions of Proline and Hydroxyproline Isolated from Collagen with Use of Nitrous Acid

Fraction	Ash	Chlorides	Ammonia Nitrogen	Total Nitrogen Found	Total Nitrogen Calculated**	l(-)Proline	Hydroxyproline
Hydroxyproline (Expt. No. 1)	16.1	0.0	0.00	5.63	5.55	8.6	42.1
Proline*** (Expt. No. 1)	7.0	0.3	0.00	9.11	7.84	50.9	15.4
Hydroxyproline (Expt. No. 2)	13.6	0.0	0.00	6.65	7.54	16.6	51.7
Hydroxyproline (Expt. No. 3)	11.9	0.0	0.00	7.75	7.60	17.3	51.5
Proline*** (Expt. No. 3)	7.1	1.4	0.00	9.40	7.00	47.7	11.2

*In grams per hundred grams of material dried sixteen hours at 60°C in vacuo.

**Calculated from the per cent nitrogen in the per cents proline and hydroxyproline as found by analysis.

***Analysis for hydroxyproline was made on a different part of the sample which accounts for the discrepancy between the nitrogen found and calculated figures.

Discussion

It is obvious that none of the fractions is pure. The presence of proline in the hydroxyproline in each case is not too surprising since we made no attempt at further purification of the same. More ethanol may have been required to remove the proline in toto. There is also the possibility that the crude hydroxyproline should have been extracted more than once with absolute ethanol to facilitate proline removal. Inability to make a material balance (ash plus l(-)proline plus hydroxyproline plus ammonia equal one hundred) indicates that organic impurities are still present in each fraction. These are probably the deaminates which, acting as weak acids, could quite conceivably account for the presence of hydroxyproline in the proline. The appreciable quantities of ash pose a problem. Qualitative tests indicated the ash in all cases to be essentially phosphates which would seem to indicate that the vegetable charcoal (containing 2.24 per cent ash which was predominately

phosphates), used in the various decolorizing treatments, was the source of this contaminant(s). The practically complete absence of chlorides seems to indicate that silver carbonate treatment is an effective means of removing chloride ions.

The excellent material balance in regard to total nitrogen in the case of the hydroxyproline fractions seems to indicate that the methods of analysis are reliable. It would also appear that racemization of neither amino acid had taken place during processing. This observation appears to be a positive one in the case of the proline and by analogy hydroxyproline though no positive proof has been established in the case of the latter. A nitrogen balance was not expected for the proline fractions since practically all of the best material was used for the other analyses and only the scrapings of the dishes were available for the hydroxyproline analyses.

The method is not perfect in any sense but the yields are good and a many-fold concentration of each of the desired amino acids has been accomplished. We concentrated on trying to increase yields and did not have the time available to thoroughly investigate means of purifying the crude products. Suffice it to say, considerable difficulty was always encountered when solvent precipitation was employed in an attempt to purify any of the fractions. The materials were hard to recrystallize and degradation took place most readily in many of the solvents as evidenced by color formation and decrease in yield of the substance finally obtained in the dry state.

Summary

1. A new method has been proposed for the isolation of proline and hydroxyproline from collagen.

2. The procedure involves treating a collagen hydrolyzate with 0.3 *N* nitrous acid in the presence of an excess of one *N* hydrochloric acid at 60°C for ninety minutes, subsequently boiling off the excess liquid, extracting with concentrated hydrochloric acid, removal of residual hydrogen chloride, and finally absolute ethanol extraction to yield two crystalline moieties.

3. In three similar experiments, good yields of each amino acid were obtained although the products were not pure.

Acknowledgment

The author gratefully acknowledges the encouragement of the Staff of the Tanners' Council Laboratory, particularly Dr. R. M. Lollar, under whose supervision this investigation was carried out.

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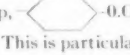
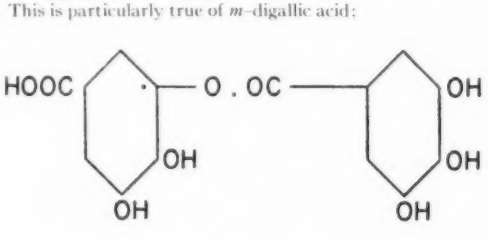
ABSTRACTS

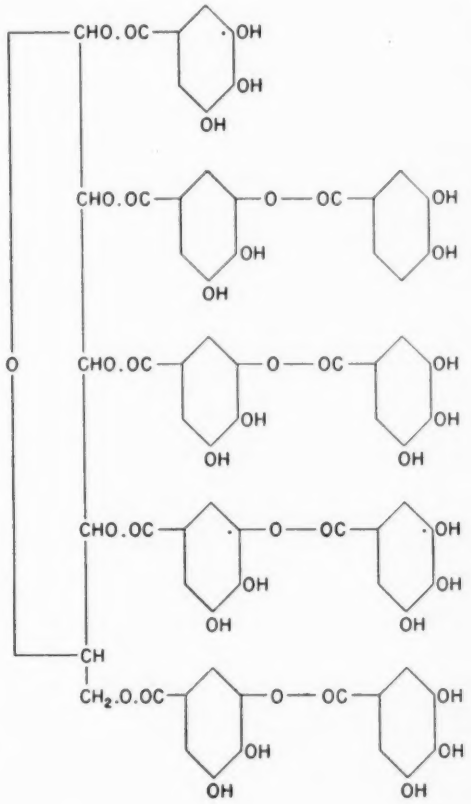
Organic Chemistry of Vegetable Tannins. By R. Ghosh. **Chapter XI of "Progress in Leather Science: 1920-1945"** *British Leather Mfrs. Assoc., London,* 1948. Vegetable tannins are classed as hydrolyzable or condensed. Hydrolyzable ones include mutual esters of phenolic carboxylic acids, esters of phenolic carboxylic acids, esters of phenolic carboxylic acids with sugars, and glucosides of depsides. Condensed tannins include hydroxy benzophenones and compounds derivable from polyhydroxy flavans. Differentiating tests are summarized as follows:

Test	Hydrolyzable tannin	Condensed tannin
$FeCl_3$	Blue Color	Green color
Digestion with dil. H_2SO_4	Gallic, ellagic acids and sugars	red ppt. (phlobaphenes)
Br. water	——	ppt.
Pine wood & HCl	——	phloroglucinol reaction
Diazobenzene chloride & alkali	——	red ppt.
HCHO test	not all ppt.	completely ppt.
Pb acetate	ppt. insol. or sl. sol. in dil. acetic acid	ppt. sol. in dil. acetic acid

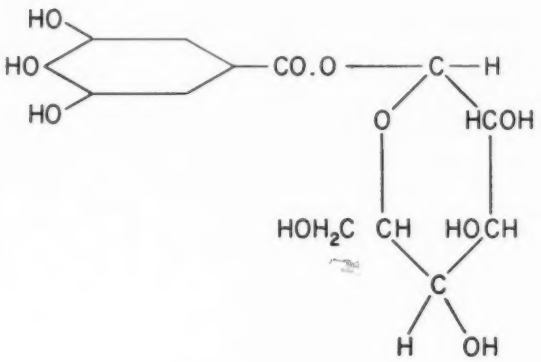
The depside group,  , is important in the constitution of hydrolyzable tannins. This is particularly true of *m*-digallic acid:



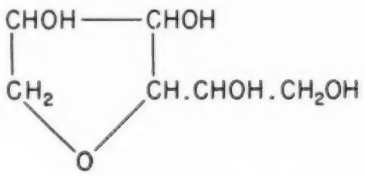
Structure of gallotannin from Chinese galls has been elucidated chiefly by Fischer, who also synthesized penta -*m*- digalloyl - β - glucose, very similar, if not identical, to natural gallotannin in elementary analysis, reactions with H_2O, gelatin, alkaloids, etc. Methylation and acetylation yield similar products, and the only slight differences, in solubility and optical rotation, can be ascribed to differences in colloidal states. Work of Karrer and others indicate that gallotannin is a mixture of 3 galloylated glycoses, the monogalloyl compound predominating. Ghosh suggests the following as one of the simplest of hundreds of possible isomeric formulas:



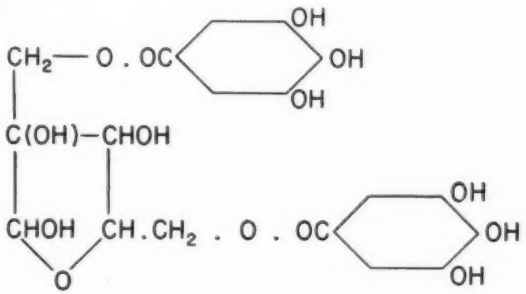
The constitution of glucogallin, also found in Chinese tannin, was proved through a synthesis by Fischer and Bergmann, and is represented as 1 galloyl - β-glucose:



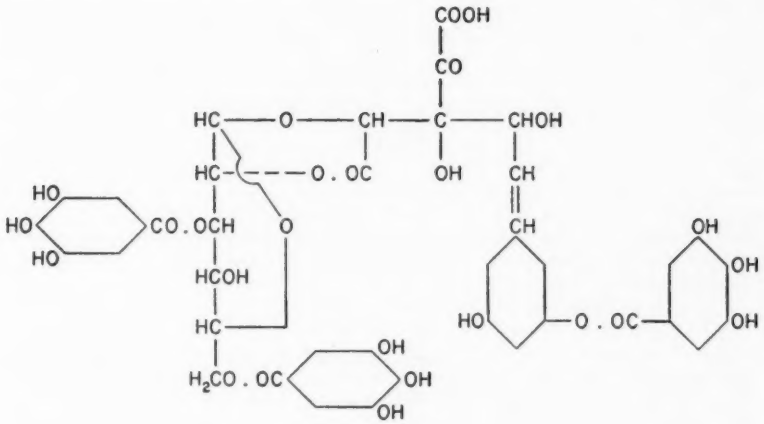
Acertannin, from leaves of the Korean maple, hydrolyzes with 5 per cent H_2SO_4 to yield 2 molecules of gallic acid and one of a crystalline sugar, aceritol, to which the following formula is provisionally attributed.



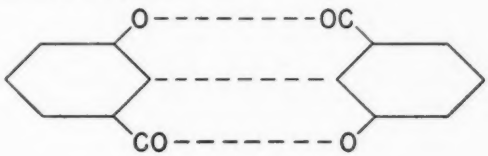
Hamameli tannin, which is crystalline, occurs in witch hazel. Freudenberg suggests the tentative formula:



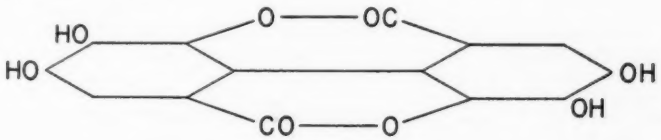
Sumac tannin requires more work to explain its structure. It resembles Chinese gallotannin to a great extent. It can be separated into at least two fractions, and probably contains 60 per cent of a pentagalloyl glucose. Chebulinic acid, a crystalline tannin, occurs with amorphous tannins in myrabolam. Freudenberg suggests the formula:



The diphenyl-demethyloloid group



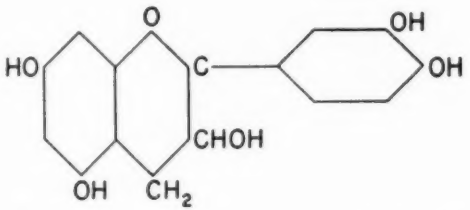
characterizes other hydrolyzable tannins, which include algarobilla, divi-divi, valonia, etc. They yield ellagic acid



on hydrolysis, and are called ellagitannins. The study of their chemistry is in its early stages. The following types of structure have been proposed: (1) a glucoside of ellagic acid, (2) an ester of luteoic acid in which the alcoholic compound is a sugar, and (3) galloyl derivatives of ellagic acid. Structural formulae so far suggested are all highly tentative.

Condensed tannins include benzophenones and flavans. Maclurin is the best example of the former. Synthesis has proved it to be pentahydroxy benzophenone; the tannin is probably a condensed product of several maclurin molecules.

Flavans include several commercially important tannins, cutch, mimosa (wattle), and quebracho. Some light on their structure has been obtained from study of catechin, a non-tannin occurring in gambier. Catechin, on heating in water, yields a tannin and eventually phlobaphenes. Work by Freudenberg and others has established its construction as:



but the question of its transformation to catechin tannin and reds is still open. Hypotheses of Freudenberg and Russell are briefly discussed. 63 structural formulae, 81 references.

Robert B. Hobbs.

Some Properties of the Commoner Vegetable Tanning Materials, and Their Significance in the Tanning of Heavy Leather. By N. L. Holmes. Chapter XII of "Progress in Leather Science: 1920–1945." *British Leather Mfrs. Assoc., London,* 1948. The action of a tanning liquor is considered as consisting of 2 functions: the action of ions from salts and acids in modifying the untanned pelt, and the combination of the fibers thus prepared with colloidal tannin particles. Salt and acid equilibrium between pelt and tan liquor is achieved much more rapidly than penetration of tannin to the middle of the pelt, but trouble, such as drawn grain, occurs if an attempt is made to tan faster than the pelt can adjust itself to salt and acid equilibrium. Degree of plumping is a function of pH value, salt content, valency of acid, and type of salt. A counter-current process such as sole leather tanning tends to a state in which all liquors have the same content of salts. Normality of acids and salts in fresh tanning liquors is given for several tannins, of which examples are:

	150° Bk.		30° Bk.	
	Acids	Salts	Acids	Salts
Mimosa	0.09	0.14	0.02	0.03
Quebracho	0.06	0.08	0.01	0.02
Sumac	0.34	0.49	0.07	0.10
Chestnut	0.59	0.04	0.12	0.01
Myrabolam	0.80	0.24	0.16	0.05

It is important to know what level of values to work at in various stages of tannage, but many variables are involved, and these have been balanced on the basis of the tanner's experience. The research chemist still has much work to do before he can be more specific in helping the tanner.

In strong liquors the concentration of salts is usually from 0.2 to 0.5 *N*; in weak liquors, 0.13 to 0.33 *N*. At pH 3, salts must be greater than 0.2 *N*, or plumping will retard penetration of tannin. If salts are less than 0.2 *N*, pH must be higher. At the other extreme; every increment of salts between 0.2 *N* and 0.75 *N* leads to progressive loss of wet firmness. Changes of blend in the strongest liquors to modify the acid and salt balance may not be apparent until 3 times the duration of the tannage has elapsed. In hot-pitting (100°F) liquors stronger than 0.25 *N* do not cause damage to leather, and salt content may go as low as 0.1 *N*. Increases in acidity tend toward greater fixation of tannin, but may lead to danger, as will shortage of salt. In such cases case-hardening and delay in penetration will occur.

Tanning is said to be an almost completely reversible reaction. There is a progressive increase in degree of tannage with increase in concentration, such that amount of tannin fixed is proportional to a low fractional power of concentration. Tanning effect depends on surface tension of the tanning solution. Soluble substances of low molecular weight which lower the surface tension lead to deposition of less tannin in the fiber; among them are alcohol, acetone, and phenol. Soluble salts generally have the opposite effect. The extreme case is the "salting-out" effect. The value of Epsom salt in finishing sole leather is explained by this effect. Quebracho and mimosa tannins, which have a higher molecular weight than myrabolam and chestnut, also give more viscous solutions at the same concentration. This is especially true of sulfited quebracho. Valonia solutions have high viscosity because of semi-soluble matter peptized by the tannin solution, though the molecular weight is not high. Viscosity is also affected by association of tannin molecules into larger particles. Speed of tannage does not depend entirely, if at all, on molecular weight. Chestnut, valonia, and myrabolam show delay in penetration into the hide, possibly because the outer layers filter out large particles, hindering penetration; quebracho, mimosa, and mangrove do not show this delay.

Substances of large particle size in the more acid tannins are peptized and "soluble" above 100° Bk, insoluble below 75° Bk. They explain discrepancies in experimental work between results from strong and from weak liquors, and between the use of pieces of pelt and of hide powder. Phlobaphenes in catechol tannins do not behave like insolubles from pyrogallol tannins. Bisulfiting alters chemical constitution so that tendency of phlobaphenes to polymerize is reduced. Sulfited particles show less tendency to adsorption on other particles attached to tanned fibers, and so yield lower degree of tannage.

Information on chemical changes in tannin due to temperature, oxidation, pH, and enzyme action is incomplete. Increase in acidity of tan liquors may be caused by oxidation. Alcoholic or enzymatic fermentation should not be allowed in the tan yard, as even small quantities of alcohol prevent tannage to the fullest extent. Aging of vegetable leather may be a chain reaction in which cationic iron catalyzes oxidation of sulfur dioxide, which in turn oxidizes tannins and leads to oxidation and acidic decomposition of the fibers. The most suitable method of protection is addition of a water-soluble oxalate, which forms a complex ion with iron, and prevents the start of the chain reaction. 16 references.

R. B. Hobbs.

Synthetic Tanning Materials. By A. T. Hough. Chapter XIII of "Progress in Leather Science: 1920–1945." *Brit. Leather Mfrs. Res. Assoc., London,* 1948. The first synthetic tanning agent, reported by Schiff in 1871, was probably a mixture of polyhydroxy aryl sulfonic acids and sulfones. Other early work was on naphthol-formaldehyde compounds. The first practical application resulted from Stiasny's work, which led to Neradol D, a condensation product of phenol sulfonic acid and formaldehyde (HCHO). Other phenols and cresols were later used similarly. Neradol N was made by sulfonating naphthalene and condensing with HCHO, and the Ordovals by sulfonating higher cyclic hydrocarbons. Such sulfonic acids combine with basic protein groups, and, though highly acidic, do not swell the fiber. They form a stable combination with collagen and cannot be easily removed by washing with water. Work by Croad in 1923 led to syntans of higher molecular weight and fewer sulfonic groups, which gave better leather. He first condensed phenol and HCHO, then sulfonated the product; this required less H_2SO_4 than the earlier method. H_2SO_4 can be cut down still more by partial substitution of sulfonic acids. Products of this type, sulfonated Novolaks, give a fuller, but darker-colored leather.

Collagen absorbs phenol, as much as 60 per cent by weight, and resorcinol and catechol to lesser extents. This is reversible, and some gelatinization occurs. At 8 per cent concentration of phenol, shrinkage temperature is at room temperature; this indicates rupture

of collagen lattice, phenol combining with peptide groups. Pelt treated with 6 per cent phenol or 15 per cent resorcinol shows leather-like drying, but washing removes the phenol or resorcinol. Slightly soluble phenols, e. g. naphthol, have a tanning effect. Weakly sulfonated Novalaks give higher degree of tannage than strongly sulfonated ones, and are thus more suited for replacement tannins. Phenol sulfonic acid is more easily condensed in aqueous solution with water-soluble aldehydes and ketones, including glucose and lactose, but not sulfite cellulose. In alcoholic solution, HCHO and acetaldehyde, as well as sulfite cellulose, react readily, but not glucose and lactose. Tannins can be prepared from resorcinol or pyrogallol with HCHO or acetaldehyde, but they are expensive and their color deteriorates rapidly. Naphthalene sulfonic acids condensed with formaledhyde yield a harsh leather, but have uses in heavy leather manufacture.

Hydroxyl and chloride substituent groups in the naphthalene nucleus increase the absorption of syntans by collagen; a second sulfo group decreases it. Condensation with HCHO does not affect absorption of free acids but increases that of the salts. OH^- and Cl^- substituted naphthalene sulfonic acids effect a satisfactory "formation" of the fiber structure even when uncondensed; the unsubstituted acids require condensation with HCHO for this result; and the 1,6-disulfonic acid does not give it even when condensed. Absorption of syntans by collagen is closely related to tanning power, but not identical with it. Condensed sulfonic acids are completely absorbed, and sulfonates strongly so. Salts with Fe, Cr, Al, and Cu are almost as strongly absorbed as free acids; next most strongly are salts with NH_4, Ba, Ca, and Mg; and finally Na and K salts. Power of being absorbed is about proportional to molecular weight. With increasing aldehyde, absorption first increases, then decreases.

Syntans of the condensed sulfonic acid type have a hydrolytic effect on leather, though this is not dangerous in the dilutions used in the tannery, particularly in the presence of vegetable tannins, which inhibit this effect. It is decreased when the sulfo group is linked with a base, as Al or Cr. Hot concentrated syntans of this type will dissolve chrome leather shavings. Hides containing sulfonic acid syntans do not take some acid dyes well; dyes containing amido groups give best results. For those acid dyes that can be used, improved results are obtained by mordanting with dyewood extract or topping with a basic dye. Such syntans can be used with or before vegetable mordants, and are powerful mordants for basic dyes. They can be used instead of formic or other acid for "driving on" acid and direct dyes. Syntans speed up vegetable tannage by combining with collagen, suppressing swelling, and retarding combination of hide with tannin. They peptize larger tannin aggregates and insolubles, and lighten color. They release organic acids in early tan liquors, but some form dark stains with lime. Failings of early syntans included excessive acidity and hydrolytic action on pelt, poor tanning power and low yields, rapid darkening of leather color, and high mineral ash content. Use of phenol ethers instead of phenol produced light-fast syntans. Linking of urea-formaldehyde resins with cresol or naphthalene improves color and resistance to light. Dioxy-diphenyl-sulfone has been used for the same purpose. Modern syntans are quite light-fast, less acid, produce a fuller leather, and do not prevent uptake of dyes. Unfortunately they are sensitive to salts, so that pickled goods cannot be tanned directly. A class of syntans designed to replace vegetable tannins is derived from sulfite cellulose, by condensation with phenolaldehyde resins or their sulfonic acids or sulfones, or with similar naphthol or resorcinol compounds. Such materials have good tanning properties and are economically sound. These newer types, with numerous hydroxy groups, are similar to the weakly acidic groups of vegetable tannins rather than the older, strongly acid syntans. Some are less highly dispersed than vegetable tannins. The ratio tan/total-soluble, is greater than 0.6. Mineral ash content is low, pH about 3 to 4. Some are very sensitive to iron salts. Leathers tanned with them show no rotting after 10 years' storage.

Official methods of tannin analysis are misleading for syntans. Examination should include proportion of organic material to salts, and tans to non-tans; behavior when heated

to dryness; effect on clarifying vegetable extracts; and small tanning experiments. It is also desirable to determine the dependence on the pH of the amount of "tan" absorbed by hide powder, and the shrinkage temperature.

(A summary of B.I.O.S. Final Reports Nos. 240 and 762, on German syntans, is included as an addendum.)

23 references. R.B.H.

Extractives from Ponderosa Pine Bark. By. E. F. Kurth and J. K. Hubbard. *Ind. Eng. Chem.*, **43,** 896 (1951). In the Pacific Northwest there are available annually approximately 400,000 tons of ponderosa pine bark having a tannin content of 5.6 to 11.4 per cent, and wax content of 5 per cent on the dry weight of the bark. Reducing sugars amount to 2-4 per cent. Total hydroxyl groups present in the tannin amount to 22.2 per cent, phenolic hydroxyl groups 13.2 per cent and aliphatic hydroxyl groups 9.0 per cent respectively. The tannin is regarded as a possible substitute for chestnut.

The Water-Pollution Problem. By L. Cox. *Amer. Dyestuffs Reporter*, **40,** 228 (1951). The author does not take the idealistic viewpoint that all streams should be restored to their original purity, but to the contrary feels that each stream should be brought to a state of cleanliness consistent with the demands made on it. He regards the polution problem as one requiring the support of municipalities and industries if it is to be solved. For industry to properly support the project there are certain steps which it must take, listed as (1) Development of full information about its own waste and to take necessary corrective action. (2) Education of its employees. (3) Cooperation with municipal officials. (4) Cooperation with Interstate and Federal control agencies. (5) Keeping the public advised concerning the problem and the progress which is being made.

Production of Protease by Cultivation of Aspergillus Oryzae on Wheat Bran. By M. E. Maxwell. *Australian J. Appl. Sci.* **1,** 348 (1951). Attempts to produce proteolytic enzymes for use in the fellmongering industry from those species which had previously shown to be responsible for loosening wool gave so little promise of success that attention was turned to the cultivation of molds possessing gelatinase activity. Of 43 species and strains of molds cultivated on steamed wheat bran, *Aspergillus flavus-orygae*, strain 292-4795, yielded culture extracts possessing the highest gelatinase activity. Optimum growth and enzyme production by this strain was obtained on sterilized bran, containing 60 per cent water, when spread in layers not exceeding 2 cm. in depth. The bran was inoculated with a spore suspension of the mold and incubated for 4 days at 28°C. in a saturated atmosphere. The gelatinase was readily extracted with water from the bran culture of the mold.

Fellmongering Investigations. XIII. Use of Mold Protease for Recovering Wool from Sheepskin Pieces. By E. M. Jenkins and M. E. Maxwell. *Australian J. Appl. Sci.*, **1,** 363 (1950). Wool is recovered from sheepskin pieces or low grade whole skins by complete digestion of the skin tissues with mold protease. After grading, fresh skin pieces are washed to remove blood and gross dirt, and dry skin pieces are soaked 24 hours. The skin collagen is shrunk by heating the washed pieces to 75°C., preferably by a flash process, as prolonged heating adversely affects wool quality. After cooling and draining, the skin pieces are immersed in an enzyme bath prepared by extracting mold bran with water. Common salt, 2 per cent on volume of liquid, is added to inhibit growth of putrefactive bacteria and prevent tainting of the wool. In an enzyme extract, maintained at 40°C. but not circulated, complete digestion of the skin requires 4 to 6 days, according to the ratio of skin to mold bran extract.

Factors Affecting the Service Life of Leather in Wool Processing. By R. M. Koppenhoefer. *Lea. Manufacturer*, **62,** No. 4, pg. 35 (1951) Experimental procedure for determining the probable life service of leather types in wool processing is described and illustrated. It is shown that the process oil rapidly displaces the natural grease from the leather. It is further shown that some oils can accelerate the rate of deterioration because of a tanning-like action exhibited by fatty oil sulfates or mineral oil sulfonates, which are widely used as emulsifiers. This deterioration can be controlled within practical limits by restricting the concentration of such components in a soluble oil to safe levels and by control of stock oiling to eliminate excesses.

Vegetable Tanning Extracts from Waste Sulfite Liquors. By F. L. Hilbert, *Lea. and Shoes*, **121,** No. 3, pg. 12, No. 4, pg. 10 10 (1951). The author briefly describes the soda, sulfate and sulfite processes for producing paper pulp. The sulfite process is the only one to yield a residual liquor useful in the tanning industry.

Reclaiming Leather Dust. By T. A. Dickinson. *Lea. and Shoes*, **121,** No. 4, 14 (1951). Leather dust or flour from the buffing operation constitutes a useful filler for synthetic elastomers. It greatly increases the abrasion resistance of rubber products without loss of flexibility. When used in thermosetting plastics fabrication of moldings and casts with more flexural strength and less weight is possible as compared with wood flour and fabric fillers. Semi-artificial leathers, composed of leather dust and polyvinylchloride resins are tough and flexible. Leather dust compounded with phenol-formaldehyde and polyester resins is suitable for the compression molding of gaskets, packings and other articles of varying degrees of rigidity. Water soluble strip coatings with improved scratch resistance for use as masks in the spray finishing of industrial products have been made by combining leather dust with polyvinyl-alcohol emulsions. Artificial suede finishes on leathers are made by spraying leather dust on the leather surface first made tacky with primer coatings. Comparison of properties of plastic with wood flour and leather dust filler, respectively, follows.

	Plastic with wood flour filler	Plastic with leather dust filler
Sp. Gr	1.25	1.15
Tensile Strength-psi	4,000	10,000
Modulus of Elasticity psi X 105	5 – 7	8 – 9
Compressive strength psi	12,000	16,000
Flexural strength psi	9,000	15,000
Izod Impact Strength foods pounds per inch	0.3	0.6
Heat Distortion, °F.	250	250
Water Absorption	0.2	0.3
Burning Rate	Low	Chars - doesn't burn
Chemical Inertness	High	High
Pigmentation	Most opaque colors	Most opaque colors

Mold Resistant Leather Treatments. Latest Specifications for Civilian and Military Leathers. By F. O'Flaherty. *Lea. and Shoes*, **121,** No. 7, pg. 12 (1951). The Surgeon General has approved 0.3 per cent para-nitrophenol in leathers which come in

close contact with human skin. The same applies to tetra-chlorohydroquinone, but this material cannot be incorporated in the leather during tannery operations. Paranitrophenol is soluble in alcohol and oils. The alcoholic solution may be added to the chrome or vegetable tanning liquors, or to the fat liquor. It can be dissolved in the stuffing mixture, or in the oils of the fat liquor and incorporated in the leather in this manner. Workmen handling para-nitrophenol should wear respirators and gloves, as it has a tendency to discolor the skin when soap is used in washing. Finished leathers can be treated with paranitrophenol by immersing them in an oil-solvent-paranitrophenol bath. A practical method for testing leathers for para-nitrophenol appears in *This Journal* 45, 728 (1950).

Making Leather with Sound Waves. By T. A. Dickinson, *Lea. and Shoes*, **121,** No. 7, pg. 8, (1951). The suggestion is made that ultrasonics may be used to speed up tanning.

Astringency Problems with Water Soluble Organic Tanning Materials. I. Influence of Particle Size of Tanning Material on the Purity Curve. By A. Küntzel and H. Grunewald. *Dzs Leder* **1,** 206 (1950). Astringency resembles the affinity of classical chemistry but is a qualitative, not a quantitative, property. This is related to the fact that commercial tannin is a mixture of components having differing affinities for hide powder. The tannin mixture can be divided into true tannin, weakly astringent semitannin, and nontannin. The total astringency of the mixture is influenced in various ways by the components. The true and semi-tannins have a more or less definite tanning action. The nontannins, on the other hand, behave indifferently or cause swelling of the hide. A distinction must be made between the acid swelling of the lower fatty acids (lactic, acetic, etc.) and hydrotropic swelling by undissociated acid molecules and phenolic nontannins. These two types of swelling have a great influence on the takeup of tannin. Astringency is therefore a summation of a complex phenomenon whose individual factors can be tested and explained. For the present work syntans rather than the similar but more complex vegetable tanning materials were used. The results were expressed as purity curves obtained by detannizing solutions of increasing concentration with hide powder by the filter method, calculating purity (tannin as percentage of soluble solids) and plotting purity against concentration. The purity of a natural tannin rises to a constant value as the concentration of the analytical solution is increased whereas the purity of a syntan rises to a maximum, then decreases. Küntzel and Bosse have postulated that the true tannins penetrate and combine with the hide powder while the semitannins are larger and only deposit on the surface of the powder. To test this view Novolaks of different particle size were prepared and then sulfonated, the assumption being made that sulfonation did not alter the particle size. Three Novolaks, with degree of condensation of 0.7 (1 mol phenol : 0.7 mol formaldehyde) were made. Novolak O, with the smallest particles, was made by heating at 100°, with stirring, 100 grams of phenol and 1 gram of oxalic acid until the odor of formaldehyde disappeared (12 hours). Novolak S, with larger particles, was made by using hydrochloric acid as catalyst (2 ml. of 18 per cent HCl per 100 grams of phenol). Yield of O was 79 per cent and of S, 87 per cent of theoretical. A different type of Novolak (Novolak N) was made by condensing the phenol and formaldehyde in a concentrated aqueous solution of β-naphthalenesulfonic acid, this acid acting both as catalyst and as emulsifying agent. Particle size was determined by fractional precipitation from alkaline solution by addition of sulfuric acid. The first fraction (precipitate) contained 60.7 per cent of the total Novolak for O, 70.9 per cent for S, and 73.9 per cent for N. Molecular weight of dissociated electrolytes can be measured by diffusion or dialysis only in the presence of a high concentration of an indifferent electrolyte but this electrolyte would salt out Novolak. The molecular weight of unsulfonated Novolak was determined by dialysis in 96 per cent alcohol. The following molecular weight values were found: Novolak O, 140; Novolak S,

309; Novolak N, 1025; the first fraction (acid precipitation) of Novolak S, 476; second fraction, 394; third fraction, 320. The purity curves for the three Novolaks differed only slightly. In view of the great difference in particle size, it is improbable that the drop in the curve at higher concentrations is caused by overcondensed particles.

II. Influence of the Sulfo Group on the Astringency of Tanning Sulfonic Acids of the Phenolnovolak Type. *Das Leder* **1,** 259. The tanning action of phenolnovolaks is known to decrease as degree of sulfonation increases. By reducing the degree of sulfonation the properties of phenolic syntans can be improved until they have the character of replacement tannins. It seemed possible therefore that the semitannins of low affinity for hide powder were oversulfonated Novolak particles. To test this assumption two methods were used. First, water soluble phenol condensation products, free from sulfo groups, were prepared and examined. The second method was to separate tannin and semitannin from Novolak by fractional detannization, and then to determine the degree of sulfonation of each fraction. A water soluble syntan was made from resorcinol and formaldehyde (molecular ratio 2 : 1) by heating for 5 hours on a water bath with hydrochloric acid as catalyst. On dilution with water the product became cloudy but redissolved at low concentrations. The purity curve resembled those for chestnut or pine extracts in that it did not drop at higher concentrations. Semitannins were absent in this unsulfonated product. For the separation of true tannins and semitannins by fractional detannization, 300 cc. of the tannin solution was shaken 3 minutes with 3 grams of hide powder than filtered on a Buchner funnel. The filtrate was treated as before with additional 3 gram portions of hide powder until the filtrate was colorless. The hide powder cakes were washed by dispersing them in 100 cc. of water, then filtering. The following four tanning materials were used; resorcinnovolak, ordinary quebracho, Tanigan extra B, and sulfonated phenolnovolak. The first two materials, which were not sulfonated, were colorless in from 2 to 4 detannizations, the sulfonated materials only after 6 or 7 detannizations. The hide powder wash waters from the sulfonated materials were more highly colored than those from the unsulfonated materials. Only the first two hide powder fractions were tanned, and the second was not as well tanned as the first. By analysis of the hide powder fractions from a sulfonated material, the degree of sulfonation of the first fraction was found to be 22.3 mol per cent and of the fifth and sixth fractions (semitannins) 36.9 mol per cent. The semitannins are strongly hydrophilic because of oversulfiting and therefore have low astringency. In the filter method of tannin analysis, the semitannin is not all retained by the hide powder and it appears as if large amounts of tannin were passing through into the filtrate but this is not so as all true tannin is retained. The actual weight of semitannin taken up by hide powder is small; semitannins thus resemble dyes. I.D.C.

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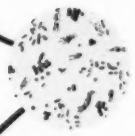

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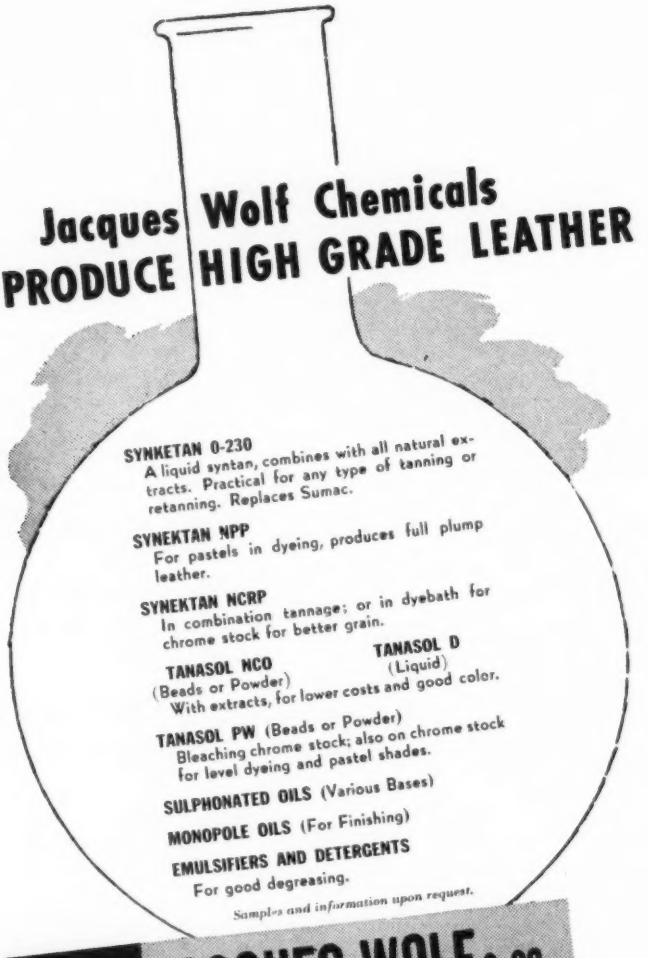

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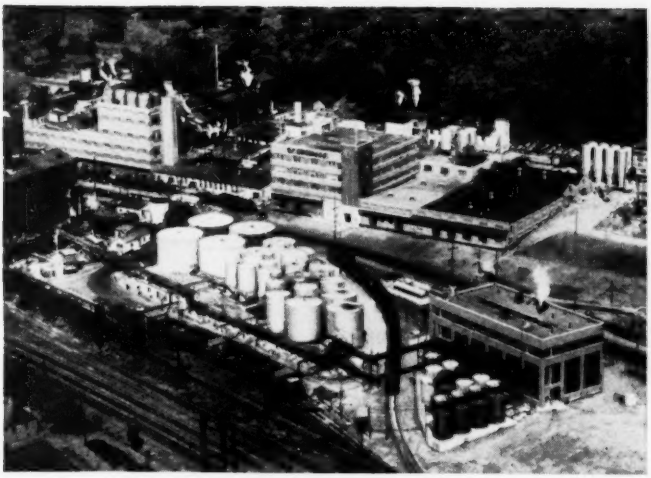

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